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UNITED STATES DEPARTMENT OF THE INTERIOR

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William P. Clark, Secretary

BUREAU OF MINES
Robert C. Horton, Director

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere, standard	lb/ft^3	pound per cubic foot
Btu	British thermal unit	min	minute
°C	degree Celsius	mL	milliliter
cm	centimeter	mL/h	milliliter per hour
ft	foot	mm	millimeter
ft^3	cubic foot	pct	percent
ft/min	foot per minute	ppm	part per million
g	gram	psi	pound (force) per square inch
gal/min	gallon per minute	psig	pound (force) per square inch, gauge
g/L	gram per liter		
h	hour	std ft^3/h	standard cubic foot per hour
in	inch	wt pct	weight percent
kW	kilowatt		

REFRACTORIES FOR DRY ASH COAL GASIFIERS

By L. Y. Sadler III,[1] H. Heystek,[2] Nancy S. Raymon,[3]
and Timothy A. Clancy[2]

ABSTRACT

This report summarizes the findings of a 9-yr research program, sponsored by the U.S. Department of Energy and conducted by the Bureau of Mines, to evaluate refractory liner materials for coal gasifier reactors. Commercially available refractories were exposed to coal gasifier reactor environments, reproduced in the laboratory with a high-temperature, high-pressure test facility, followed by extensive postexposure evaluation. Thirty-six castable or gunnable refractories and cements and 24 refractory brick were evaluated. The behavior of castable refractories reinforced with stainless steel fibers was also examined. Gas environments that were evaluated included steam, H_2, CO_2, CO, and typical high- and low-Btu gas mixtures. Exposure pressures ranged from 100 to 1,000 psig, temperatures from 500° to 1,100° C, for periods from 50 h to 2,000 h. In some exposures, sodium and/or potassium hydroxide were introduced in order to simulate a high-alkali environment. It was found that intermediate- and low-alumina refractories produced from domestically available raw materials, rather than high-alumina refractories produced from imported raw materials, gave the best service as liner materials and that alkali attack was probably not a serious problem with most refractories. Based on the results of this program, good choices of refractory liner materials for gasifier reactors can be made.

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INTRODUCTION

Most coal gasifier reactor designs call for an inner lining of refractory material to reduce heat losses and lower containment vessel wall temperatures. Temperatures at the lining hot face can range from about 700° to above 1,000° C, and pressures from 1 atm to greater than 1,000 psig, depending on the particular gasification process. Depending on the gasification temperature and coal ash properties, the lining hot face can be coated with molten ash. The gas composition in all gasification processes includes steam, carbon monoxide and carbon dioxide, hydrogen, methane, ammonia, and hydrogen sulfide, with the relative amounts depending on the specific gasification process (1).[4] Alkalies from the coal, and in some cases purposely added as catalyst, are also present. The selection of a refractory liner material that will offer an acceptable service life in such a severe environment is a critical element in the success of a coal gasification plant.

Until recently, based on experience with linings in ammonia plant secondary reformers where process conditions are similar to those in most advanced coal gasifiers, it was suggested that hot-face refractory linings of very high alumina (>95 pct) content and low iron oxide ($\approx$0.2 pct) and silica ($\approx$0.3 pct) contents would be required (2-5). Because the production of these refractories requires imported bauxite as a raw material, the Bureau of Mines initiated research in mid-1974 to identify the most cost-effective refractory lining materials and to determine whether the lower alumina refractories that can be made from domestic raw materials could be used.

From mid-1975 to mid-1983 the research was sponsored by the U.S. Department of Energy.[5] During this period 36 commercial refractory castables, ramming mixes, and plastics and 24 refractory brick were tested in a high-temperature, high-pressure test facility, designed and constructed at the Bureau's Tuscaloosa Research Center. Interim reports covering part of the work on refractories as well as the design of the reaction vessel were made in 1979 and 1981 (6-7). This report summarizes the results obtained on all the refractories evaluated over the 9-yr life of the program.

ACKNOWLEDGMENTS

TEST EQUIPMENT

The high-temperature, high-pressure test unit consisted of a controlled-atmosphere sample container having a working volume of about 0.3 ft³. The unit was capable of operating continuously at 1,000 psi and 1,100° C. A schematic diagram of the unit is shown in figure 1. The sample container was made from a 24-in-long by 6-in-diam, schedule

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[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

FIGURE 1. - Schematic of high-temperature, high-pressure specimen exposure facility.

80 310 stainless steel seamless pipe. Three independently controlled iron-Chromel[6] heating elements, each capable of delivering 2.6 kW, were used to heat the container. The cylindrically shaped heaters enclosed the sample container and were themselves surrounded by 3 in of Kaolite 2300 LI insulating castable refractory cast against the low-alloy steel wall of the pressure vessel. The pressure vessel, which had a breech-type closure, was designed to withstand 3,000 psi at a wall temperature of 350° C. Circular baffles, welded to the pressure vessel wall, extended through the castable insulation to within 1/2 in of the exterior of the heaters to interrupt convection currents at the vessel wall. Tightly packed KAOWOOL ceramic fiber blanket insulation filled the lower portion of the pressure vessel below the sample container. Figure 2 shows the furnace with the upper portion of the pressure vessel removed.

The metal pressure vessel shell temperature was maintained at about 120° C by circulating 3 gal/min cooling water at 25° C through a copper coil bonded to the exterior of the pressure vessel shell. Inert gas (argon) was introduced into the annular area between the sample container and the pressure containment vessel. The inert gas was automatically maintained at a pressure about 10 psi higher than the pressure of the reactive gas atmosphere inside the sample container. Thus the unit was designed to operate so that the hot walls of the sample container would not be subjected to stresses due to a high pressure differential. In addition, should a leak develop in the sample container, inert gas would flow into the container, preventing reactive gas flow from the container into the insulating lining and onto the heating elements. Figure 3 is a schematic diagram showing the operation of the automatic differential pressure (ΔP) control system. The differential pressure sensor converted the measured ΔP to a pneumatic signal,

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[6]Reference to specific products does not imply endorsement by the Bureau of Mines.
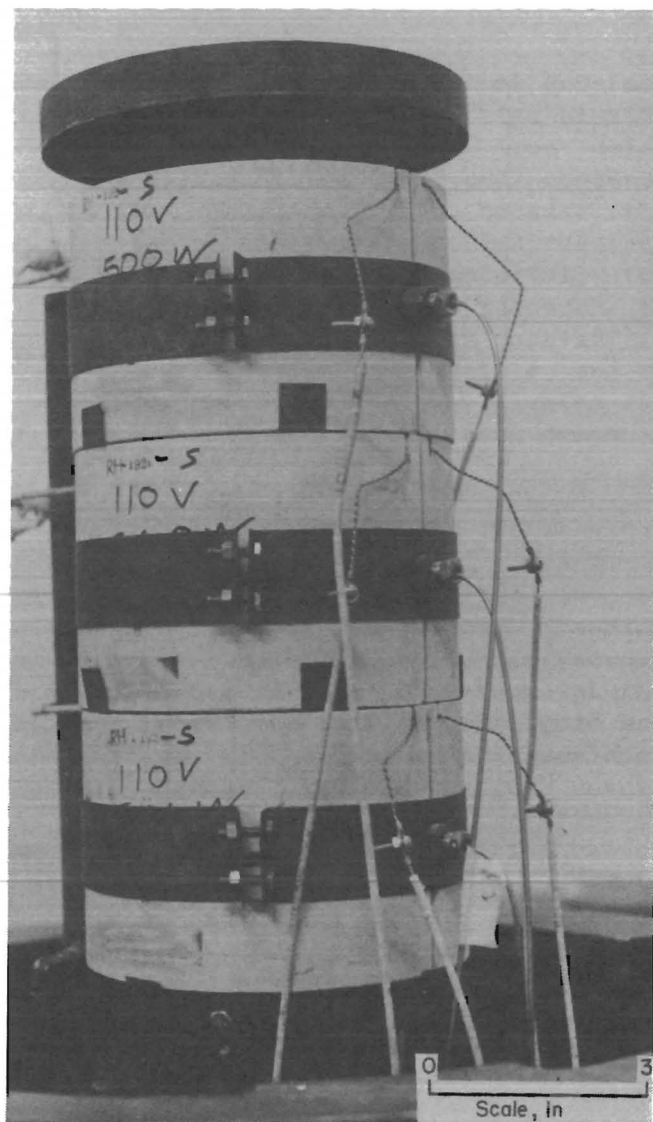
FIGURE 2. - Sample container surrounded by heating elements.

which was fed to the ΔP controller-indicator. This pneumatic device, with proportional and integral control, compared the measured ΔP with the set point value, sending an appropriate pneumatic signal to control valves 1 and 2. If the measured ΔP was higher than the desired value (set point), then control valve 2 opened while control valve 1 closed. Conversely, if the ΔP was too low, control valve 1 opened while control valve 2 closed. When ΔP was at the set point, both valves were closed. Approximately 5 std ft^3/h of inert gas was passed through the insulating space during the course of normal operation of the ΔP control
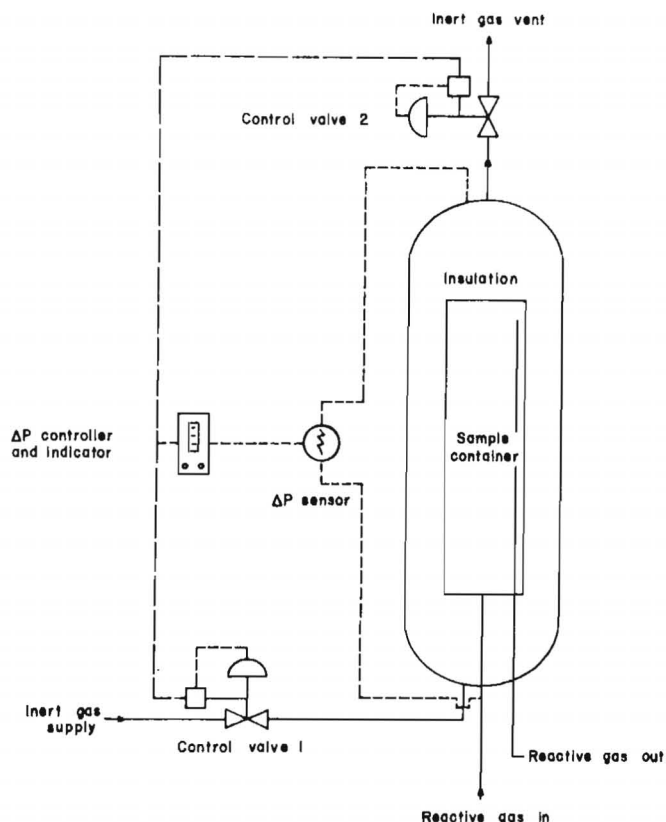
FIGURE 3. - Automatic differential pressure control system.

system. High-purity argon was used an an inert backfill gas because of its chemical and metallurgical inertness at high temperature and because it has a relatively low thermal conductivity when compared to helium.

Reactive gases were dispensed from compressed gas cylinders and delivered at 1,000 psi, from adjustable gas pressure regulators, to the sample container. If a steam-free sample treatment atmosphere was desired, the reactive gas passed directly from the regulator to the sample container. However, if steam was to be one of the reactive gas components, the gas was first fed through a stainless steel sparger at the bottom of the steam generator and bubbled up through the liquid in the steam generator, shown in figure 4, becoming saturated with steam at the temperature of the liquid in the generator. The steam generator was a modified autoclave designed for 2,000-psi operation at 350° C. Thus, the steam partial pressure in the reactive gas fed

to the sample container was controlled by the temperature maintained in the steam generator. The liquid level in the steam generator was measured by a resistance-type single-level sensing system. A high-pressure positive displacement liquid metering pump (with adjustable stroke for delivery from 16 to 160 mL/h), automatically started and stopped by the level control system, kept the liquid at a preset level as steam continuously left the generator with reactive gas on its way to the sample container. H_2S and NH_3 were introduced, when required, with makeup water to the steam generator as an aqueous $(NH_4)_2S$ solution of the desired H_2S-NH_3-steam ratio. For example, if it was desired to expose the samples to an atmosphere of 40 pct steam, 1 pct H_2S, 2 pct NH_3, and 57 pct other reactive gases at 1,000 psig, the dry reactive gas regulator would be set at 1,000 psig, the steam generator temperature set at 224° C, and a 6 wt pct aqueous $(NH_4)_2S$ solution charged to the makeup water feed tank. When subjecting the refractory samples to an atmosphere of only steam, no other gas was admitted to the generator. Steam was generated at a pressure determined by the generator temperature and injected directly into the furnace sample container. For a steam atmosphere at 1,000 psig, the required steam generator temperature was 285° C.

The reactive gas was usually introduced to the sample container from the bottom and traveled upward past the test specimens and into a standpipe with its inlet at the top of the sample container. After flowing down through the standpipe, the gas was vented from the vessel. Figure 5 shows the test unit control panel. Figure 6 shows the controlled-atmosphere furnace with the removable pressure containment vessel head being lowered over the sample container.

Inert gas leaving the furnace was cooled, metered, and discharged, with periodic analysis by gas chromatography to detect the presence of internal leaks. The reactive gas leaving the sample container was cooled, passed through a liquid-gas separator, metered, and

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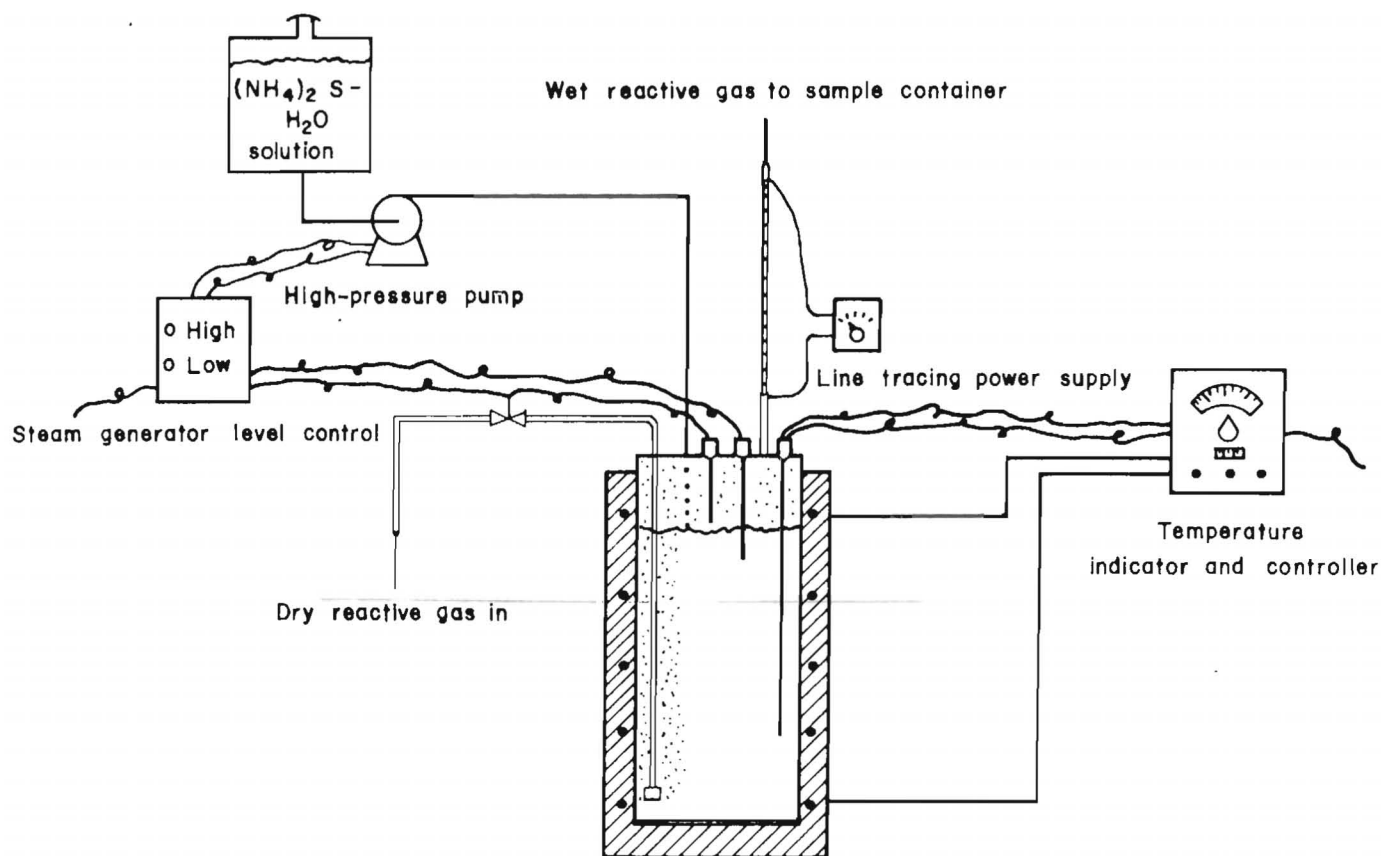
FIGURE 4. - Schematic of steam generator system.

vented. Its composition was also monitored to check for leaks of inert gas into the sample container and to monitor exiting reactive gas composition.

The pressure vessel, steam generator, sample container, gas-liquid separators, and water makeup pump were all protected from overpressurization by either safety relief valves or rupture discs. The high-temperature, high-pressure furnace, steam generator, and most of the connective piping were separated from the control room by an 8-in steel-reinforced concrete wall. High-capacity ventilation fans were operated continuously in the pressure vessel area to prevent possible buildup of toxic or flammable gases that

could have resulted from small, undetected leaks in connective piping. Continuous automatic monitors for CO, H_2, and H_2S were wired to an audible alarm system to give advance warning of potentially dangerous leaks into the furnace and control rooms. An automatic shutdown system was activated once steady state was reached to prevent damage to the equipment had a component failure occurred. The entire system was operated for periods of up to 2,000 continuous hours with only minor adjustments being required of the operator. Figure 7 is a flowsheet of the monitoring and shutdown system and shows the sequence of corrective actions that were to be automatically taken in the event of a failure.

TEST PROCEDURE

The experimental work consisted primarily of exposing nearly 60 commercial refractories to coal gasification atmospheres, followed by postexposure

characterization of these test specimens. The refractory castables are listed in tables 1 and 2, and the brick are listed in table 3. Some of the

TABLE 1. - Properties of commercial CA-bonded refractory castables and CA cements

Trade name	Classification	Cement	Aggregate	Bulk density, lb/ft^3	Chemical composition, wt pct						
					Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	K_2O+Na_2O
CASTOLAST G......	95-pct-Al_2O_3 dense castable..	High-purity CA.	Tabular alumina.	163	95.3	0.3	0.2	Trace	3.3	0.1	0.2
GREENCAST-94.....	...do.....................	...do..	...do...........	163	94.5	.1	.2	ND	4.5	.1	.3
PLICAST L-2284...	...do.....................	...do..	...do...........	190	94.4	3.4	.1	ND	1.2	Trace	.1
GREENKON-30......	85-pct-Al_2O_3 dense castable..	...do..	...do...........	175	84.5	9	1	2.5	1.9	Trace	.2
LO-ERODE.........	60-pct-Al_2O_3 dense castable..	...do..	Calcined fire clay.	127	57.9	32.1	.9	1.3	6.7	.2	.6
LOABRADE.........	55-pct-Al_2O_3 dense castable..	...do..	...do...........	128	53.4	38	2.6	1.6	4.6	.2	.7
RESCO 17E........	...do.....................	...do..	...do...........	130	55.5	36.7	.7	1	5.5	.2	.3
H.S. BRIKCAST B.F.	50-pct-Al_2O_3 dense castable..	Intermediate-purity CA.	...do...........	130	49.7	38.3	1.1	2.2	7	.2	.1
HyMOR 3000.......	...do..	...do..	...do...........	145	49.9	44.3	1.1	1.2	2.2	.1	.4
BLAST FURNACE CASTABLE 122 N.	50-pct-Al_2O_3 gunning mix.....	High-purity CA.	...do...........	135	50	43.1	1.1	2.3	3.2	.1	.2
Q-GUN 30-50......	...do..	...do..	...do...........	127	53.2	40.1	.9	1.5	3.5	.1	.7
BLAST FURNACE GUN CASTABLE.	45-pct-Al_2O_3 gunning mix.....	...do..	...do...........	131	45.5	47.3	1.4	1.2	3	.3	.8
KAOCRETE D.......	45-pct-Al_2O_3 dense castable..	Low-purity CA..	...do...........	128	44	39	5.4	1.7	10.2	Trace	Trace
Q-CRETE 25 H.S...	...do..	...do..	...do...........	131	46	36.8	3.4	1.2	11.6	.3	Trace
KAOLITE-3300.....	95-pct-Al_2O_3 insulating castable.	High-purity CA.	Bubble alumina..	68	94	.5	.2	ND	4.6	.1	.5
PLICAST LWI BUBBLE CAST.	...do..	...do..	...do...........	70	94.6	.5	.2	Trace	4.5	.1	.1
KAST-O-LITE-30...	60-pct-Al_2O_3 insulating castable.	...do..	Expanded fire clay.	90	59.5	33.5	.7	.7	4.5	.4	.7
GREENCAST-26-L....	...do..	...do..	...do...........	54	58.5	30	.8	.8	8.2	.1	2
PLICAST LWI 28...	55-pct-Al_2O_3 insulating castable.	...do..	Calcined fire clay.	74	54.2	36.3	.8	.1	5.7	.2	1.5
LITECAST 75-28...	50-pct-Al_2O_3 insulating castable.	...do..	...do...........	86	54.7	35.4	1.3	1.2	4.9	.3	1.1
PLASTIC INSULCRETE.	40-pct-Al_2O_3 insulating castable.	Low-purity CA..	...do...........	80	38.5	45.4	3.3	.8	10.7	.2	.6
PLICAST LWI 20...	...do..	...do..	...do...........	52	38.6	31.5	5.4	1.5	19.5	.8	1.4
VSL-50...........	30-pct-Al_2O_3 insulating castable.	Intermediate-purity CA.	Expanded fire clay.	60	32.5	54.5	.7	.7	8	.4	1.5
CA-25...........	78-pct-Al_2O_3 CA cement.......	High-purity CA.	NAp.............	113	73.1	.5	.3	Trace	16.7	.1	.4
REFCON..........	60-pct-Al_2O_3 CA cement.......	Intermediate-purity CA.	NAp.............	94	58	5.6	1.5	ND	33.5	ND	ND

NAp Not applicable. ND Not determined.

TABLE 2. – Properties of commercial phosphate- and chromate-bonded refractory castables and ramming mixes

Trade name	Classification	Aggregate	Bulk density, lb/ft³	Chemical composition, wt pct									
				Al_2O_3	SiO_2	Fe_2O_3	Cr_2O_3	TiO_2	CaO	MgO	K_2O+Na_2O	P_2O_5	ZrO_2
AA-22.........	Phosphate-bonded 90-pct-Al_2O_3 dense castable.	Tabular alumina.	187	86.6	0.8	0.07	ND	ND	0.1	2.8	Trace	5.1	ND
BRIKRAM 90R...	Phosphate-bonded 90-pct-Al_2O_3 ramming mix.	...do....	172	87.9	7.9	.2	ND	0.04	.22	.1	0.2	3.9	ND
KAO-PHOS 93...	...do...............	...do....	170	93	.2	.1	ND	.2	.7	ND	.1	5.6	ND
SHAMROCK 888..	Phosphate-bonded 85-pct-Al_2O_3 ramming mix.	...do....	210	85.5	1.9	.5	9.7	ND	ND	ND	.4	2.0	ND
LAVALOX X-8...	Phosphate-bonded 85-pct-Al_2O_3 chrome plastic.	...do....	193	84.6	.2	.04	10.2	.01	ND	ND	.2	4.6	ND
KRITAB........	...do...............	...do....	195	84.6	1.8	.2	9.1	ND	.01	.1	.3	4.1	ND
LAVALOX B-135[1]	...do...............	...do....	ND	67.0	ND	ND	32.0	ND	ND	ND	ND	ND	ND
HW 23-75......	Phosphate-bonded 60-pct-Al_2O_3 ramming mix.	ND.......	163	56.4	36.5	1	ND	1.7	.1	.1	.3	3.9	ND
KEMRAM........	Phosphate-bonded 40-pct-Cr_2O_3 ramming mix.	ND.......	190	23.7	1.4	23.5	40.4	ND	2.8	10	ND	.9	ND
VALLE 623.....	Phosphate-bonded 80-pct-Al_2O_3 zircon ramming mix.	Tabular alumina.	192	82	11.8	ND	ND	ND	ND	1.2	ND	1	5
GUNTAPITE 382.	Chromate-bonded 90-pct-MgO ramming mix.	Periclase	170	.3	3.2	1.1	1.2	ND	1.6	92.4	Trace	ND	ND
F-264.........	...do...............	...do....	160	.3	3	1.1	1.5	ND	2.8	91	ND	ND	ND

ND Not determined.
[1]Experimental mix.

TABLE 3. – Properties of commercial refractory brick

Trade name	Classification	Bond	Mineralogy	Bulk density, lb/ft³	Chemical composition, wt pct											
					Al_2O_3	SiO_2	Fe_2O_3	Cr_2O_3	TiO_2	CaO	MgO	K_2O+Na_2O	SiC	Si_3N_4	P_2O_5	ZrO_2
SR-99	99 pct Al_2O_3	Sintered	Alpha alumina.	196	99.7	0.1	0.1	ND	Trace	Trace	Trace	0.1	ND	ND	ND	ND
99 AD	...do	...do	...do	192	98.6	.6	.2	ND	0.02	0.1	Trace	.2	ND	ND	ND	ND
ARCO 90	90 pct Al_2O_3	...do	...do	194	87.1	11.9	.3	ND	.04	.2	0.1	.2	ND	ND	ND	ND
KRICOR	...do	...do	...do	186	91.6	8	.2	ND	Trace	Trace	Trace	.2	ND	ND	ND	ND
RUBY	90 pct Al_2O_3 chrome	...do	...do	198	89.5	.1	.1	9.5	Trace	.3	.5	Trace	ND	ND	ND	ND
SERV-M (852Z)	90 pct Al_2O_3	...do	...do	201	87.9	.5	.5	9.8	ND	ND	ND	.4	ND	ND	1.0	ND
CORAL BP	80 pct Al_2O_3	...do	...do	177	82.3	8.3	1.3	ND	2.6	ND	ND	ND	ND	ND	5.5	ND
MULFRAX W	...do	...do	Mullite	ND	78.5	20.6	.4	ND	Trace	.1	Trace	.2	ND	ND	ND	ND
X-13233[1]	70 pct Al_2O_3 spinel bonded.	...do	Spinel	ND	72	ND	ND	ND	ND	ND	28	ND	ND	ND	ND	ND
UFALA TI	60 pct Al_2O_3	Sintered, tar-impregnated.	...do	161	59.7	36.3	1	ND	2.6	.2	.1	.1	ND	ND	ND	ND
MONOFRAX K-3	60 pct Al_2O_3 chrome	Fused-cast.	...do	244	60.4	1.8	4.2	27.3	ND	ND	6	.3	ND	ND	ND	ND
UNICHROME	50 pct Al_2O_3 Zr-Cr.	...do	Mono ZrO_2, Al_2O_3-Cr_2O_3 solid solution.	197	48.7	11	ND	15	ND	ND	ND	ND	ND	ND	ND	24.0
BISON	50 pct Al_2O_3	Sintered	Mullite, quartz, cristobalite.	151	47.9	48.3	1.1	ND	2.3	.1	.1	.2	ND	ND	ND	ND
HW 1-77	...do	...do	...do	150	47.6	48.5	1.3	ND	2.2	.1	.1	.2	ND	ND	ND	ND
KX-99	45 pct Al_2O_3	...do	...do	143	44.4	49.9	1.6	ND	2.5	.3	.2	.8	ND	ND	ND	ND
VARNON BF	...do	...do	...do	146	43.4	52.1	.9	ND	2.4	.3	.2	.7	ND	ND	ND	ND
MAGNEL	90 pct MgO spinel bonded.	...do	Periclase.	178	8.4	.7	.3	ND	ND	.8	89.8	ND	ND	ND	ND	ND
CORHART 317	70 pct MgO spinel bonded.	Fused-cast.	...do	192	31.9	.2	.1	ND	ND	.5	67.1	.2	ND	ND	ND	ND
NUCON 60	Mag-chrome	Sintered	...do	190	13.2	1.5	6.3	14.5	ND	.7	63.8	ND	ND	ND	ND	ND
GUIDON	...do	...do	...do	203	5.4	1	12	18.1	ND	.8	62.7	ND	ND	ND	ND	ND
GR-200	...do	...do	...do	196	13.1	1.9	6.8	19	ND	.8	59	ND	ND	ND	ND	ND
DIBOND 50	...do	...do	...do	193	16.7	2.3	7.8	19.6	ND	.9	52.7	ND	ND	ND	ND	ND
MONOFRAX E	Chrome-mag	Fused-cast.	Spinel	255	4.7	1.3	6.1	79.7	ND	ND	8	.1	ND	ND	ND	ND
REFRAX 20	Silicon carbide	Sintered[2]	Silicon carbide.	163	.3	.5	.3	ND	ND	.2	ND	ND	75.0	23.4	ND	ND

ND Not determined.   [1]Experimental mix.   [2]Specimens representing direct-, oxynitride-, and silicate-bonded material.
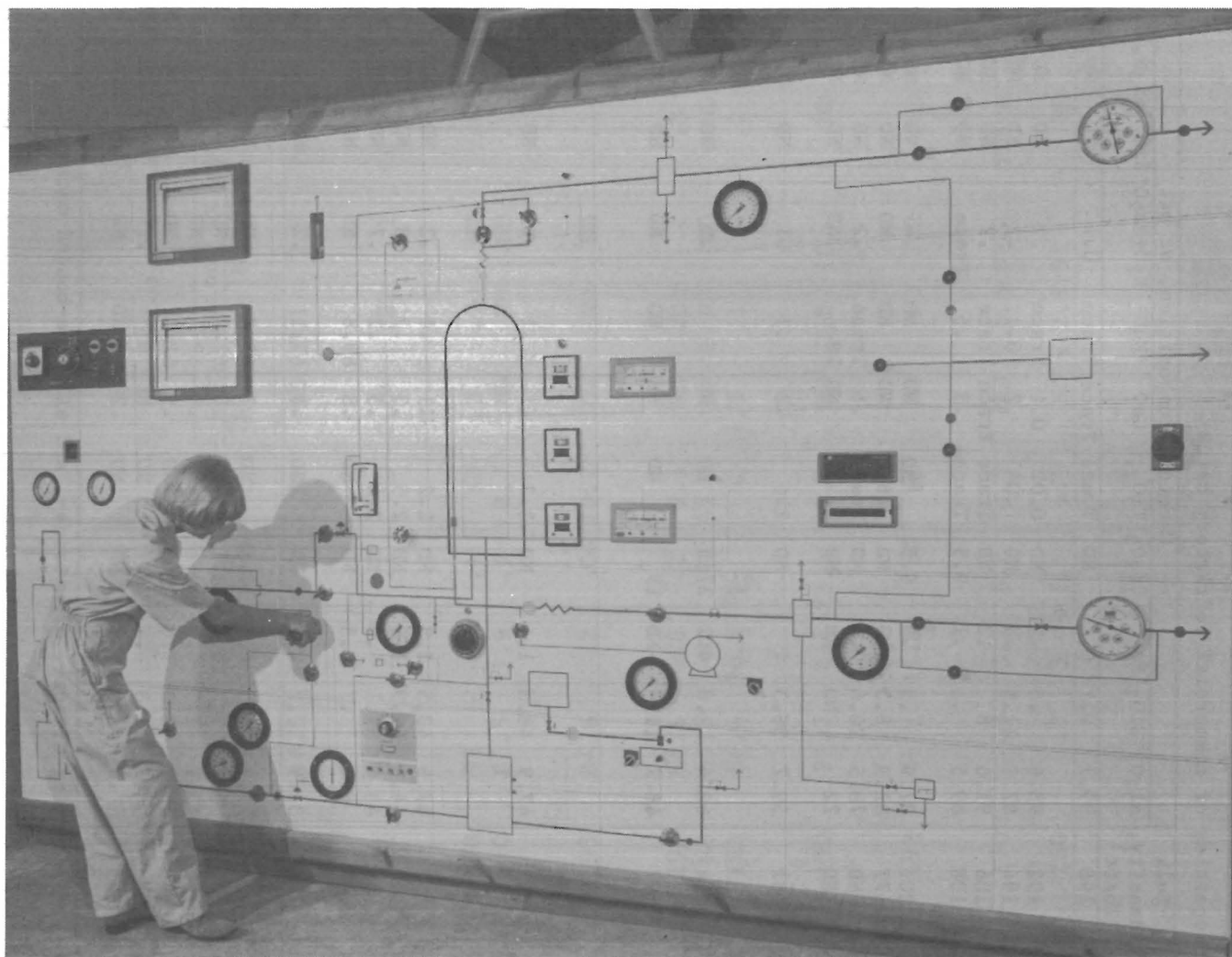
FIGURE 5. - High-pressure controlled-atmosphere furnace main control panel.

refractories listed in these tables were not included in all exposure tests. Refractory castables were prepared in accordance with manufacturer's guidelines except where specifically noted. Brick specimens were cut from commercially available products using a diamond saw.

INDIVIDUAL GASES

The first tests conducted were designed to determine which gases in typical coal gasifier atmospheres were most aggressive toward gasifier hot face refractory liner materials. Exposures to H_2, CO, CO_2, and steam were made at 1,100° C to accelerate corrosion rates. In these exposure tests, the gas flow rate through the sample container was maintained at about 6 std ft^3/h. Exposure conditions are shown in table 4.

Properties of specimens after testing were compared to properties of identical specimens that had been fired in air at a pressure of 1 atm at the same temperature and for the same length of time. Flexural and compressive strengths, abrasion resistance, and bulk densities were determined in accordance with ASTM guidelines. In addition, chemical analyses and X-ray diffraction (XRD) phase identification were made on both air-fired and exposed specimens.
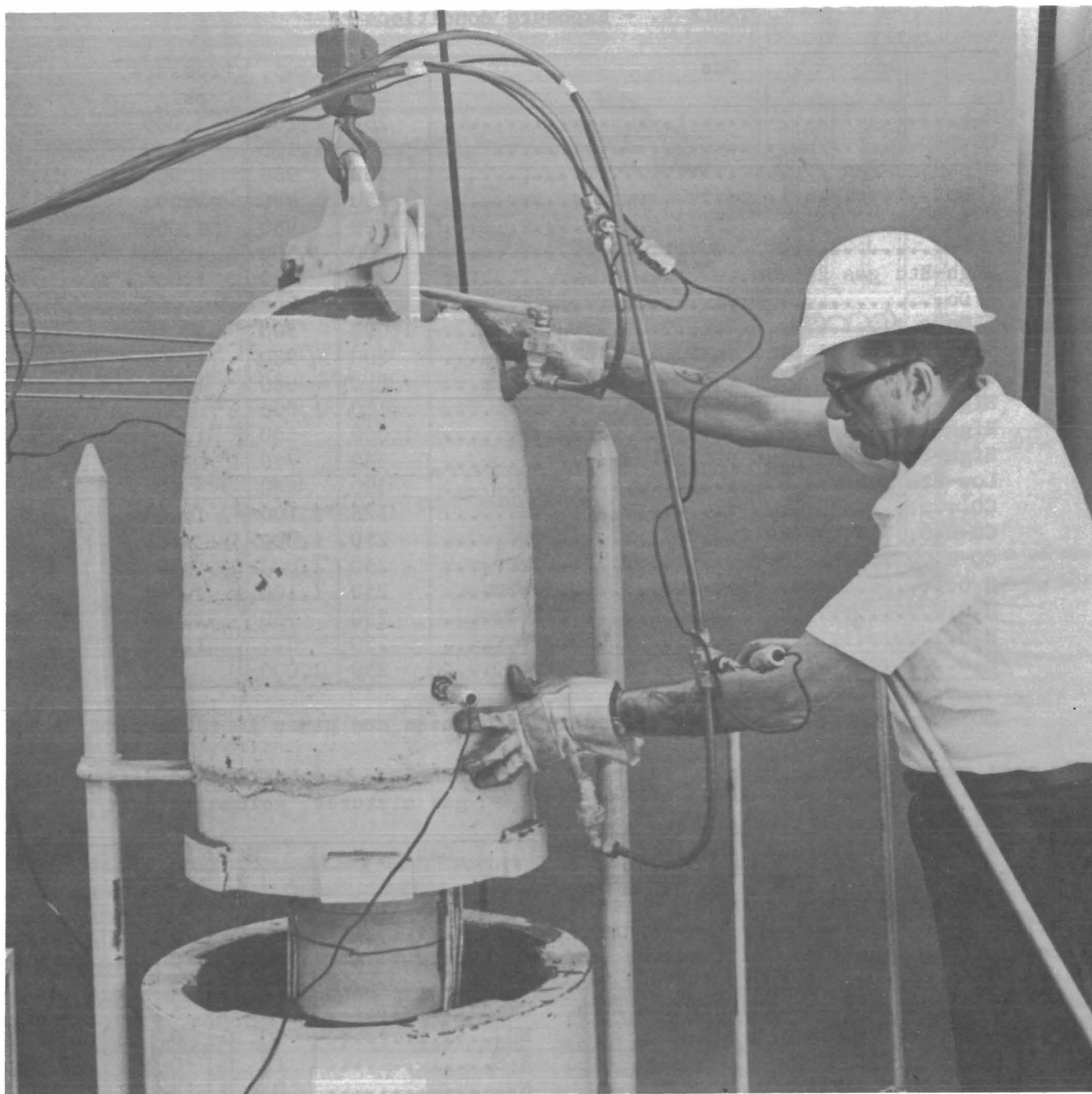
FIGURE 6. - High-pressure controlled-atmosphere furnace.

TABLE 4. - Exposure conditions

Gas	Time, h	Temp, °C	Pressure, psig
H_2..................................	250	1,100	1,000
CO_2..................................	250	1,100	800
High-Btu gas 1...........................	160	980	1,000
Do..................................	250	980	1,000
Do..................................	1,000	980	1,000
Do..................................	1,000	500	1,000
High-Btu gas 2...........................	250	980	1,000
Do..................................	250	760	1,000
Do..................................	1,000	500	1,000
High-Btu gas 1 plus sodium and potassium...	200	980	1,000
High-Btu gas 2 plus sodium and potassium...	250	980	1,000
High-Btu gas 2 plus sodium.................	100	1,000	360
High-Btu gas 3...........................	1,000	500	1,000
High-Btu gas 4 plus potassium..............	250	720	500
Low-Btu gas.............................	500	980	400
CO..................................	125	1,100	1,000
$CO-H_2O$, 3.5 ratio..........................	250	1,000	105
$CO-H_2O$, 7.0 ratio..........................	250	1,000	105
H_2O..................................	250	1,100	1,000
H_2O..................................	250	980	1,000
H_2O..................................	250	815	1,000
H_2O..................................	250	1,000	105

NOTE.--Compositions of high- and low-Btu gases are given in table 5.

In most cases only compressive strength data on 1- by 1- by 2-in bars are presented, since flexural strength and abrasion resistance increased whenever compressive strength increased and vice versa. At least four specimens of each material were exposed, and the significances of the observed differences in average compressive strength values between air-fired and exposed samples were examined statistically.[7]

GAS MIXTURES

Exposure to High-Btu Gas

After the initial tests in which refractories were exposed to individual gas atmospheres were completed, extensive tests were run using the gas mixtures shown in table 5. These mixtures were

TABLE 5. - Composition of different gas mixtures, volume percent

Gas	High Btu				Low Btu
	1	2	3	4	
H_2O.............	38	40	40	32	12
H_2.............	24	25	25	21	17
CO.............	18	18	0	6	13
CO_2.............	12	12	12	14	9
CH_4.............	5	5	5	22	5
NH_3.............	2	0	0	2	2
H_2S.............	1	0	0	1	1
N_2.............	0	0	18	2	42

considered to be typical of conditions expected in several of the proposed high-Btu gasification processes. The temperatures and pressures investigated (table 4) represent conditions at the hot face of the refractory liner in dry ash or nonslagging, high-Btu, coal gasifier reactors, and in lower temperature catalytic coal gasifier reactors. In all exposure tests, the gas flow rate across

[7]The Student's t-test at the 99-pct level of confidence was used.
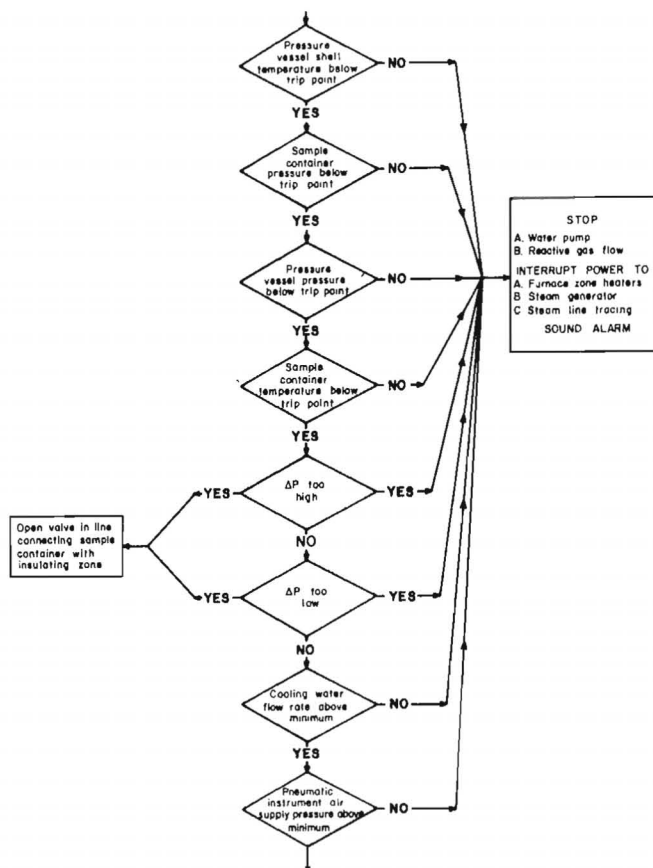
FIGURE 7. - Automatic monitoring system.

FIGURE 8. - Placement of specimens inside sample chamber in silica loss study.

the test specimens was maintained at approximately 6 std ft^3/h.

In addition to evaluating refractory specimens prepared without modification from manufacturer-supplied dry castable mixes, a considerable effort was devoted to determining the effect of stainless steel fiber additions on the properties of refractory concretes exposed to high-Btu gas 2 mixture at 980° C and 1,000 psig for 250 h. Four types of metal fibers and two alumina-based refractory castables were used in the formulation of the castable specimens. Types 310, 430, 446, and coated 446 stainless steel fibers were used, and the refractory concretes included a high-purity calcium aluminate (CA)[8] bonded 95-pct-Al_2O_3 castable and a medium-purity CA-bonded 50-pct-Al_2O_3 castable.

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[8]Within this report, conventional cement chemistry notation is used; i.e., C = CaO, A = Al_2O_3, S = SiO_2.

The metal-fiber- or wire-containing test samples were prepared in the same manner as plain castable samples except that 2 wt pct of each type of fiber (based on the castable dry weight) was dry-mixed into each refractory concrete prior to casting.

Based on reports in the literature, there was general concern about silica volatilization in low-alumina refractories in the high-temperature, high-pressure gaseous environments expected in high-Btu gasifiers. To evaluate this possibility, specimens of a CA-bonded 55-pct-Al_2O_3 dense castable, both as 1- by 1- by 2-in bars and also as minus 20-mesh material held in alumina crucibles, were placed in the sample container. Specimens of high-silica refractory insulating fibers (KAOWOOL) were also placed in the container. The placement of these specimens is shown in figure 8. Specimens of the bars and 20-mesh material were removed and replaced periodically to obtain

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samples for testing that had been exposed for 0, 50, 100, 150, 200, and 250 h to this environment.

For the final 100 h of the exposure, crushed (1/2- by 1/4-in) castable also was placed in the 1-in-ID standpipe that served as the reacting gas atmosphere inlet inside the sample container. This was done so that these specimens could be exposed to the same temperatures as, but to greater gas velocities than, the specimens in the sample container. When the crushed refractory was removed from the standpipe, it was noted whether it came from the lower, middle, or upper third of the standpipe so that the effect of gas velocity (and thus mass transfer resistance) on the volatilization and redeposition of silica could be investigated. The superficial velocity in the standpipe was calculated to be 1.4 ft/min, compared with 0.04 ft/min in the sample container.

Reports from the literature (2) indicate that carbon monoxide in typical coal gasifier atmospheres may have the potential to rapidly disintegrate iron-containing refractory lining materials under static conditions at 500° to 600° C. To substantiate the reports of CO disintegration, a series of 1,000-h exposure tests of refractories to three different high-pressure, high-Btu gas atmospheres under dynamic conditions at 500° C were run. The one mixed gas exposure was to a high-Btu gas that contained H_2S and NH_3 (gas 1, table 5). The other gas atmosphere was similar but contained no H_2S or NH_3 (gas 2, table 5); the third gas composition was the same as the second but contained N_2 in place of CO (gas 3, table 5).

Exposure to Alkali-Containing High-Btu Gas

High-Btu Gas Environment Containing Potassium and Sodium

To investigate the effect of alkali-containing high-Btu gas environments, three platinum crucibles, each holding a 2:1 by weight potassium hydroxide-sodium hydroxide (KOH-NaOH) mixture, were placed in the sample container, as shown in figure 9, and surrounded by test specimens, which were in turn separated from each other by thin alumina plates. Ten specimens of each refractory were prefired at 980° C in air for 24 h. Eight specimens from each group were placed in the sample container for exposure at 980° C and 1,000 psig. The remaining two specimens from each group were soaked for 24 h in a water solution containing 500 g KOH and 250 g NaOH (2.17 g K_2O/gNa_2O) in 600 mL water and oven-dried at 125° C for 24 h. One specimen from each group thus impregnated with alkali was placed in the sample container to be exposed with the eight specimens previously mentioned. The remaining alkali-impregnated specimens were fired in air at 980° C and 1 atm for 200 h for comparison purposes.

Further testing was done to determine effects of alkali-containing high-Btu gas environments on the high-temperature

KOH-NaOH

KEY

Impregnated specimen

KOH-NaOH

Nonimpregnated specimen

KOH-NaOH

Thermocouples

Alumina balls

Gas inlet   Gas outlet
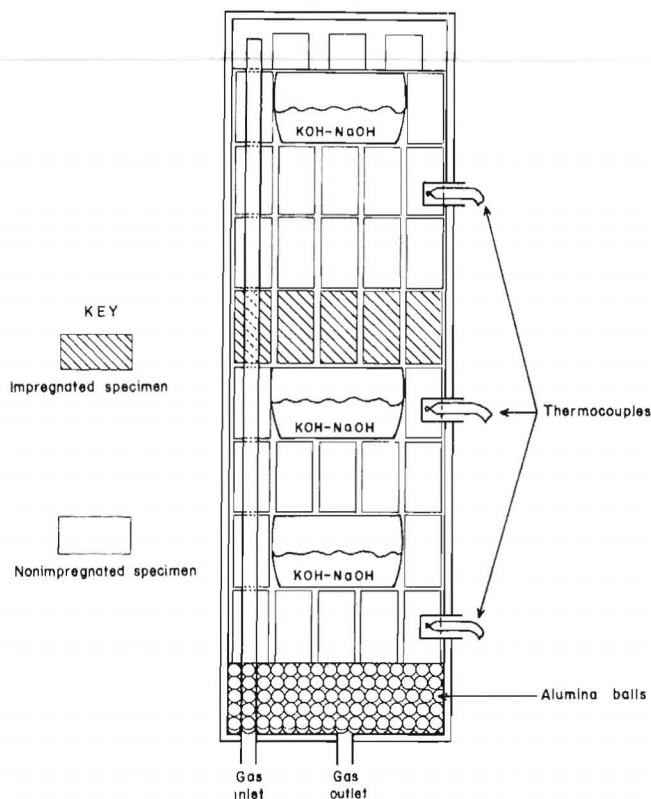
FIGURE 9. - Sample placement in sample container for potassium and sodium containing high-Btu gas exposures.

strength properties, as measured by the hot modulus of rupture (MOR), of refractories exposed to coal gasifier atmospheres. Prefired specimens (1- by 1- by 7-in bars) of refractories were soaked for 24 h in a solution of KOH and NaOH containing 50 and 25 wt pct, respectively, of each alkali hydroxide. Half the specimens of each refractory soaked in the two solutions were exposed to a steam-containing high-Btu gas (gas 4) at 980° C and 1,000 psig for 250 h. The remaining alkali-impregnated samples were heated in air at 980° C and 1 atm for 250 h for comparison.

High-Btu Gas Environment Containing Sodium

A series of 360-psig tests to simulate conditions at the 1,000° C hot face of
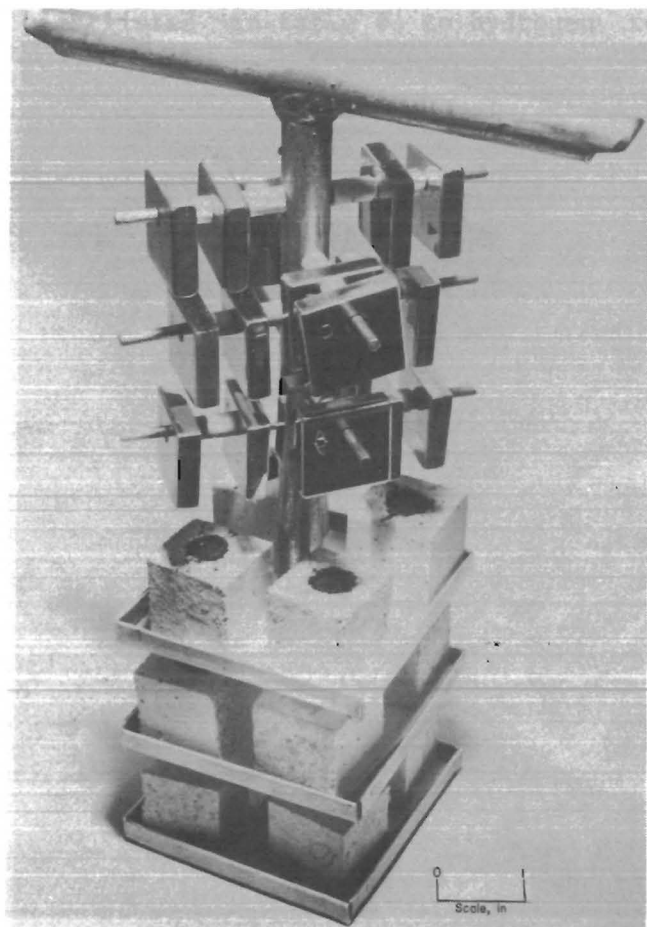
FIGURE 10. - 310 stainless steel "tree" supporting metal and refractory test coupons in CCG exposure.

the fixed-bed slagging gasifier at the U.S. Department of Energy Grand Forks Energy Technology Development Center (GFETC) was conducted. These tests were conducted because an 80-pct-Al_2O_3 refractory (MULFRAX W) cracked and spalled after 125 h of service in this gasifier. A refractory failure analysis concluded that the transport of sodium from the high-soda lignite coal during processing caused formation of beta-alumina and carnegieite with subsequent volume expansion (at least 30 pct) of the lining material.

In the tests at Tuscaloosa, samples of the 80-pct-Al_2O_3 refractory and a 45-pct-Al_2O_3 brick were subjected to the high-Btu gas 2 at 1,000° C and 360 psig for 50 h. Before the test some specimens of each refractory were soaked in a saturated solution of NaOH; crystals of NaOH were packed into holes (3/4-in-diam by 3/4-in-deep) drilled in other specimens, while char (obtained from the GFETC gasifier) was packed into holes in other refractory specimens prior to exposure. After the 50-h exposure was completed, 100-h exposures were run on refractory samples with NaOH crystals packed into holes drilled in the specimens.

High-Btu Gas Environment Containing Potassium

To evaluate refractories as gasifier liner materials for the Exxon catalytic coal gasification (CCG) system, various techniques were tried to introduce potassium to the gas composition (high-Btu gas 4, table 5) that was typical for this process. An initial 100-h test was run at 720° C and 500 psig. Test specimens were subjected to KOH vapor, to both KOH vapor and KOH liquid, and to KOH-impregnated coal in the high-Btu gas 4 atmosphere. Duplicate test specimens of each refractory were exposed to each of the three modes of alkali contact.

Shelves welded to the lower portion of a sample tree (fig. 10) supported refractory specimen cubes, including those with 1/4-in holes filled with a mixture of 20 pct KOH and 80 pct Illinois No. 6 coal. Refractory specimens were also exposed to

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molten KOH by placing them in a platinum crucible containing enough KOH so that approximately half of each sample was below the KOH liquid-vapor interface, as shown in figure 11.

During the exposure, a KOH-water solution (44.34 g/L KOH) was pumped into the test chamber on a semicontinuous basis at a rate such that if all the alkali from this source vaporized, the concentration (mole basis) of KOH vapor in the gas would have been 50 ppm.

Interruptions encountered in the initial 100-h screening test due to the pumping procedure used indicated a need to improve the method of introducing alkali vapor into the test chamber. A heavy-wall (12/16-in-OD by 5/16-in-ID) 310 stainless steel feedline was run for 11 in from the base of the sample

container down to join a 1/4-in 316 stainless steel feedline. It was hoped that any vibrations caused by the rapid vaporization of the KOH solution would not fatigue the heavy-wall feedline. Exposure conditions in this test differed from those in the previous exposure in two ways: The duration was increased to 250 h, and the primary source of alkali vapor resulted from pumping KOH solution into the test chamber, with no provision being made to produce alkali vapor by evaporation from platinum dishes containing molten KOH.

A 2,000-h exposure test of refractory and metal materials to the CCG atmosphere (high-Btu gas 4) and alkali vapor in equilibrium with char obtained from Exxon's CCG pilot plant was also run at 730° C and 500 psig. Some refractory specimens were packed in CCG char during
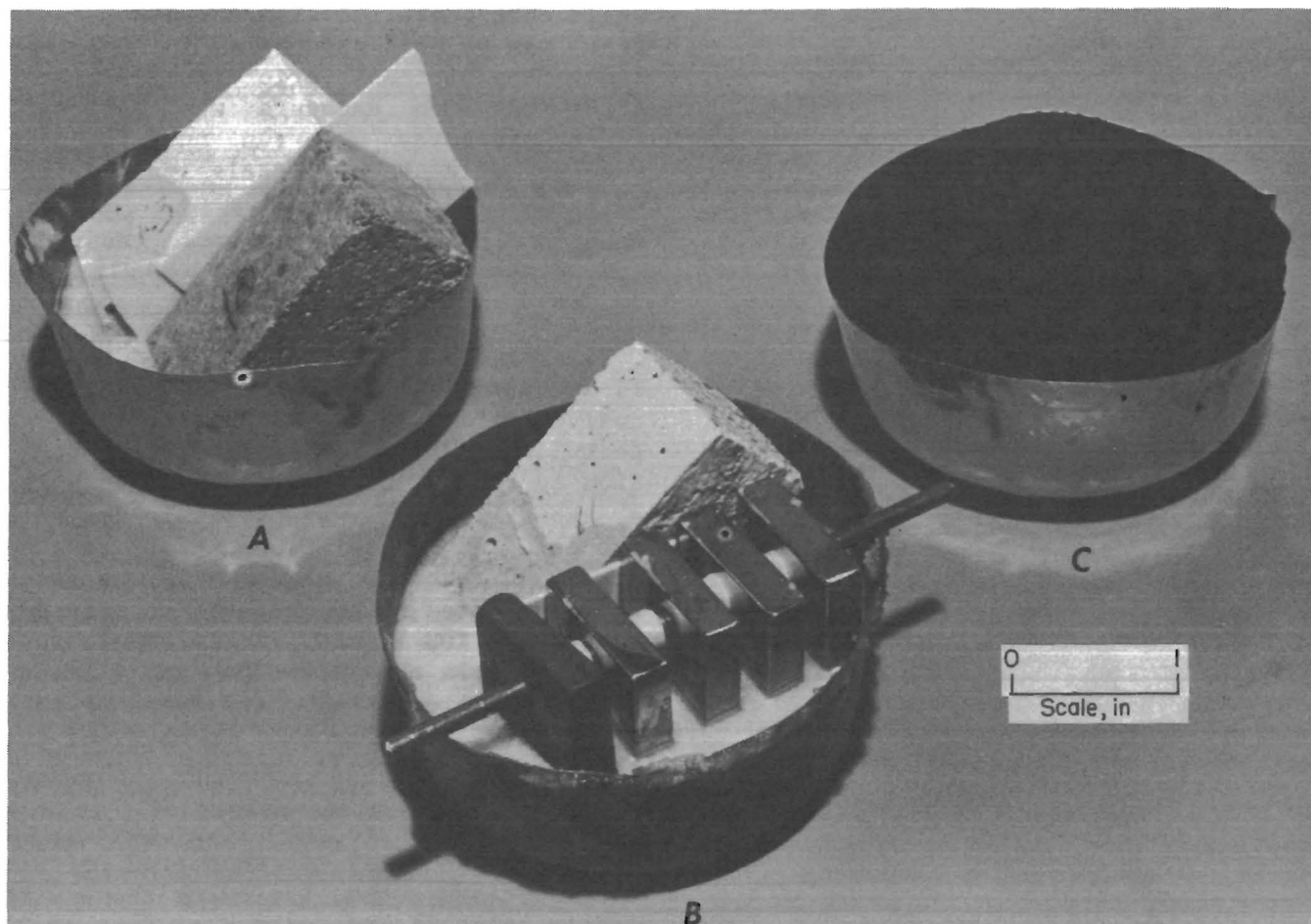
FIGURE 11. - A, Refractory specimens in KOH melt; B, metal and refractory specimens in KOH melt; C, alloy coupons in KOH-coal mixture.

exposure or had char packed into holes drilled in the specimen. The exposure was interrupted at 500-h intervals to replenish the char and to inspect the specimen exposure chamber so that severely corroded specimens could be replaced by additional specimens.

Exposure to Low-Btu Gas

For exposure to a low-Btu gas environment at 980° C and 400 psig, the dry gas mixture was introduced into the steam generator, which was maintained at 140° C in order to produce a gas containing 12 pct steam. Total gas flow rate through the container was 3.6 std ft³/h measured at 21° C and 2 psig. Two exposures to this environment were made. In one, several refractories cast from as-received dry mixes were exposed for 250 h. In the other, one lightweight and three dense refractory castables containing steel fibers were exposed for 500 h. Six different types of stainless steel fibers were used.

RESULTS AND DISCUSSION

INDIVIDUAL GASES

Exposure to Hydrogen at 1,000 psig and 1,100° C

After exposure of the refractory samples listed in table 6 to hydrogen for 250 h at 1,100° C and 1,000 psig, no visual evidence of physical changes was observed. Table 6 presents compressive strength data for this exposure. Refractories showing statistically significant differences when compared to control samples fired in air at 1,100° C for 250 h are denoted by small double-ended arrows (↔). The data show that hydrogen exposure significantly lowered the compressive strength of the CA-bonded 95-pct-Al_2O_3 dense castable and the 45-pct-Al_2O_3 brick. A statistically significant higher strength was noted for the CA-bonded 55-pct-Al_2O_3 dense castable and the 99-pct-Al_2O_3 brick.

TABLE 6. — Results of exposing refractories to hydrogen at 1,100° C and 1,000 psig for 250 h

Trade name	Classification	Compressive strength, psi [1]	
		Air fired [2]	Hydrogen
CASTOLAST G[3]....	CA-bonded 95-pct-Al_2O_3 dense castable.	3,370± 520 ↔	2,200± 260
LOABRADE........	CA-bonded 55-pct-Al_2O_3 dense castable.	1,470± 130 ↔	1,890± 200
LITECAST 75-28..	CA-bonded 50-pct-Al_2O_3 insulating castable.	1,360± 90	2,110± 140
CA-25...........	78-pct-Al_2O_3 CA cement.	11,510±2,440	8,820±1,570
BRIKRAM 90R.....	Phosphate-bonded 90-pct-Al_2O_3 ramming mix.	20,590±3,520	19,250±3,740
99 AD...........	99-pct-Al_2O_3 brick.....	8,440±3,140 ↔	12,090±2,920
ARCO 90.........	90-pct-Al_2O_3 brick.....	21,160±7,280	20,530±7,900
UFALA TI........	60-pct-Al_2O_3 brick.....	10,680±4,090	5,690±3,480
KX-99...........	45-pct-Al_2O_3 brick.....	10,960±1,890 ↔	4,050±1,020

[1]95-pct confidence intervals shown. Significant difference at 99-pct confidence level is indicated by "↔".

[2]Fired in air at 1,100° C for 250 h.

[3]The compressive strength value for CASTOLAST G was well below that reported in manufacturer's technical data sheets. A new supply of castable was obtained, and specimens were prepared that were used in later test runs, tables 11 through 29.

There was less quartz present in the insulating castable and less cristobalite present in the ramming mix after hydrogen exposure than after air firing. The P_2O_5 content of the phosphate-bonded ramming mix decreased from 3.58 to 0.03 wt pct after exposure to hydrogen without affecting strength.

Exposure to Carbon Dioxide at 800 psig and 1,100° C

The results of compressive strength determinations after exposure to carbon dioxide at 1,100° C and 800 psig for 250 h are shown in table 7. The CA-bonded 55-pct-Al_2O_3 dense castable (high-purity CA cement) increased in strength, whereas the strength of the CA-bonded 45-pct-Al_2O_3 dense castable (intermediate-purity CA cement) was reduced.

X-ray diffraction phase identification revealed that only two refractories changed appreciably in mineralogy. The insulating castable had more quartz and less anorthite after exposure to CO_2 than after firing in air, and the 45-pct-Al_2O_3 brick showed an increase in tridymite. No significant changes in bulk density were noted.

Exposure to Carbon Monoxide at 1,000 psig and 1,100° C

CO gas was fed to the sample container, but analyses of the exit gases revealed the presence of 15 to 40 pct CO_2. Extensive deposits of elemental carbon were found in the sample container upon completion of the test run, confirming CO_2 formation by the reaction $2\ CO \rightarrow CO_2 + C$.

In the first exposure, the sample container was pressurized with CO before being brought to exposure temperature. Surface spalling of the high-alumina CA-bonded castable and disintegration of

TABLE 7. - Results of exposing refractories to carbon dioxide
at 1,100° C and 800 psig for 250 h

Trade name	Classification	Compressive strength, psi[1]	
		Air fired[2]	Carbon dioxide
CASTOLAST G[3]....	CA-bonded 95-pct-Al_2O_3 dense castable.	3,480± 590	2,910± 350
LOABRADE........	CA-bonded 55-pct-Al_2O_3 dense castable.	1,500± 190 ↔	2,270± 240
KAOCRETE D......	CA-bonded 45-pct-Al_2O_3 dense castable.	4,440± 200 ↔	3,390± 440
LITECAST 75-28..	CA-bonded 50-pct-Al_2O_3 insulating castable.	1,880± 270	1,680± 250
CA-25...........	78-pct-Al_2O_3 CA cement.	9,420±3,130	9,020±1,110
AA-22...........	Phosphate-bonded 90-pct-Al_2O_3 dense castable.	6,060± 860	6,520± 500
BRIKRAM 90R.....	Phosphate-bonded 90-pct-Al_2O_3 ramming mix.	19,080±4,390	16,330±4,200
99 AD...........	99-pct-Al_2O_3 brick.....	7,250±1,820	8,680±1,690
ARCO 90.........	90-pct-Al_2O_3 brick.....	25,530±3,820	22,750±8,360
UFALA TI........	60-pct-Al_2O_3 brick.....	9,480±2,660	8,490±1,830
KX-99...........	45-pct-Al_2O_3 brick.....	10,960±1,890	12,400±1,440

[1]95-pct confidence intervals shown. Significant difference at 99-pct confidence level is indicated by "↔".
[2]Fired in air at 1,100° C for 250 h.
[3]The compressive strength value for CASTOLAST G was well below that reported in manufacturer's technical data sheets. A new supply of castable was obtained, and specimens were prepared that were used in later test runs, tables 11 through 29.

the insulating castable indicated that CO attack had occurred, probably at temperatures below 1,100° C. A subsequent 125-h CO exposure was run in which the sample container was brought to 1,100° C before CO was admitted, and at the termination of the exposure, all CO was purged from the container before the temperature was reduced. As shown in table 8, no significant strength changes were noted in any of the exposed specimens tested after this exposure. No differences in mineralogy between the air-fired and CO-exposed specimens were detected by XRD, and no significant differences in bulk density were detected in any of the refractory specimens tested. The carbon found in the sample container at the completion of this exposure could have formed at lower temperatures in the piping leading to the container and been transported to the container by the flowing gas.

Exposure to Steam at 1,000 psig and 1,100° C

After exposure to steam at 1,000 psig and 1,100° C for 250 h, a glass coating about 0.5 mm thick was observed on some of the alumina plates separating the test specimens and on portions of the sample container walls. Energy-dispersive X-ray analysis of the glass coating identified silicon, aluminum, iron, potassium, calcium, manganese, and phosphorus, in order of decreasing abundance.

Table 9 shows the effect of steam exposure on the compressive strength of the various materials before and after exposure. Whereas the high-alumina dense castable showed a significiant strength reduction, the lower alumina CA-bonded refractory castable and the 60-pct-Al_2O_3 brick had significantly higher strengths after exposure to steam than after firing in air at the same temperature for the same time.

Data in table 10 indicate that vapor-phase silica migration did occur. High-silica (low-alumina) refractories lost silica, whereas some low-silica refractories gained in silica content, originating in all probability from the higher silica refractories and reaching the low-silica specimens through vapor-phase

TABLE 8. - Results of exposing refractories to carbon monoxide at 1,100° C and 1,000 psig for 125 h

Trade name	Classification	Compressive strength, psi[1]	
		Air fired[2]	Carbon monoxide
CASTOLAST G[3]....	CA-bonded 95-pct-Al_2O_3 dense castable.	3,060± 700	3,960± 2,320
LOABRADE........	CA-bonded 55-pct-Al_2O_3 dense castable.	1,330± 130	1,890
LITECAST 75-28..	CA-bonded 50-pct-Al_2O_3 insulating castable.	1,110± 110	ND
CA-25...........	78-pct-Al_2O_3 CA cement.	7,880±1,220	ND
BRIKRAM 90R.....	Phosphate-bonded 90-pct-Al_2O_3 ramming mix.	15,400±4,630	15,760±11,200
99 AD...........	99-pct-Al_2O_3 brick.....	8,440±3,140	11,140± 9,290
ARCO 90.........	90-pct-Al_2O_3 brick.....	21,160±7,280	22,640± 2,660
UFALA TI........	60-pct-Al_2O_3 brick.....	10,680±4,090	10,560± 9,070
KX-99...........	45-pct-Al_2O_3 brick.....	6,750±1,920	7,580± 2,250

ND Not determined.   [1]95-pct confidence intervals shown.
[2]Fired in air at 1,100° C for 125 h.
[3]The compressive strength value for CASTOLAST G was well below that reported in manufacturer's technical data sheets. A new supply of castable was obtained, and specimens were prepared that were used in later test runs, tables 11 through 29.

TABLE 9. – Results of exposing refractories to steam at 1,100° C and 1,000 psig for 250 h

Trade name	Classification	Compressive strength, psi[1]		
		Air fired[2]	Steam	
CASTOLAST G[3]....	CA-bonded 95-pct-Al_2O_3 dense castable.	3,370± 520 ←→	1,420± 220	
LOABRADE........	CA-bonded 55-pct-Al_2O_3 dense castable.	1,470± 130 ←→	5,480± 920	
LITECAST 75-28..	CA-bonded 50-pct-Al_2O_3 insulating castable.	1,360± 90 ←→	4,860± 420	
BRIKRAM 90R.....	Phosphate-bonded 90-pct-Al_2O_3 ramming mix.	20,590±3,520	15,070±8,250	
99 AD...........	99-pct-Al_2O_3 brick.....	8,440±3,140	8,180±4,460	
ARCO 90.........	90-pct-Al_2O_3 brick.....	21,160±7,280	25,020±2,690	
UFALA TI........	60-pct-Al_2O_3 brick.....	10,680±4,090 ←→	17,430±2,590	
KX-99...........	45-pct-Al_2O_3 brick.....	10,960±1,890	11,620±2,420	

[1]95-pct confidence intervals shown. Significant difference at 99-pct confidence level is indicated by "←→".
[2]Fired in air at 1,100° C for 250 h.
[3]The compressive strength value for CASTOLAST G was well below that reported in manufacturer's technical data sheets. A new supply of castable was obtained, and specimens were prepared that were used in later test runs, tables 11 through 29.

TABLE 10. – Effect of steam exposure at 1,100° C and 1,000 psig for 250 h on silica content of refractories

Trade name	Classification	Silica content, wt pct	
		Air fired[1]	Steam
CASTOLAST G.....	CA-bonded 95-pct-Al_2O_3 dense castable.	0.3	1.9
LOABRADE........	CA-bonded 55-pct-Al_2O_3 dense castable.	38.0	37.4
LITECAST 75-28..	CA-bonded 50-pct-Al_2O_3 insulating castable.	35.4	34.3
BRIKRAM 90R.....	Phosphate-bonded 90-pct-Al_2O_3 ramming mix.	7.9	6.9
99 AD...........	99-pct-Al_2O_3 brick.....	.6	1.2
ARCO 90.........	90-pct-Al_2O_3 brick.....	11.9	10.5
UFALA TI........	60-pct-Al_2O_3 brick.....	36.3	34.1
KX-99...........	45-pct-Al_2O_3 brick.....	49.9	48.6

[1]Fired in air at 1,100° C for 250 h.

migration. Small differences in bulk density (the maximum being about 4 pct) were also noted.

X-ray diffraction phase identification of the dense CA-bonded concretes indicated that there was more anorthite and less CA_2 and cristobalite after exposure to steam than after firing in air. The insulating refractory castable showed an increase in mullite, with decreases in quartz and kyanite, after exposure to steam. Less quartz and more tridymite were found in the ramming mix exposed to steam than in identical specimens fired in air. No differences in the mineralogy of the 78-pct-Al_2O_3 CA-cement specimens were found. Only small differences in mineralogy were observed in the 99- and 90-pct-Al_2O_3 brick, but in the 60- and

45-pct-Al_2O_3 brick more tridymite and less cristobalite were found in the specimens exposed to steam than in the specimens fired in air.

Energy-dispersive X-ray mapping of silicon for several of the 45- and 50-pct-silica brick specimens indicated that the amount of silicon near the surface of the brick exposed to steam was less than the amount in the interior of the brick, as shown in figure 12. This suggests that steam-induced silica transport from the surface of the brick had occurred.

Exposure to Steam at 1,000 psig and 980° C

An exposure temperature of 980° C was selected as typical of the actual temperatures to be expected in most second-generation coal gasifier reactors. Table 11 presents the results of a 250-h, 980° C exposure of refractory samples considered as lining material for gasifiers to 1,000-psig steam. The same general strength decrease in high-alumina

castables and high-purity cements and increase in strength of lower alumina castable seen at 1,100° C was evident at 980° C.

Following exposure to steam, the SiC test specimens were found to be totally disintegrated, and the phosphate-bonded 40-pct-chrome, 24-pct-Al_2O_3 ramming mix suffered severe strength loss. No statistically significant changes in compressive strength occurred in any of the other refractories exposed to steam as compared to identical specimens fired in air.

X-ray diffraction analyses of the refractory samples following exposure to steam showed few mineralogical differences from identical specimens exposed to air except in the cases of the two refractories affected by steam. A complex spinel (chromite) had formed in the phosphate-bonded 40-pct-chrome and 24-pct-Al_2O_3 ramming mix, and cristobalite had developed in the SiC.

TABLE 11. — Results of exposing refractories to steam at 980° C and 1,000 psig for 250 h

Trade name	Classification	Compressive strength, psi[1]	
		Air fired[2]	Steam
CASTOLAST G.......	CA-bonded 95-pct-Al_2O_3 dense castable.	9,810±1,590 ↔	7,595± 420
LOABRADE..........	CA-bonded 55-pct-Al_2O_3 dense castable.	1,920± 280 ↔	2,675± 375
H.S. BRIKCAST B.F.	CA-bonded 50-pct-Al_2O_3 dense castable.	3,090± 270 ↔	10,790± 715
CA-25.............	78-pct-Al_2O_3 CA cement......	10,355± 810 ↔	8,220± 770
SHAMROCK 888......	Phosphate-bonded 85-pct-Al_2O_3 ramming mix.	11,240±2,530	12,900±1,150
KEMRAM............	Phosphate-bonded 40-pct-Cr_2O_3 ramming mix.	14,620±1,510 ↔	5,710±1,020
RUBY..............	90-pct-Al_2O_3 chrome brick...	11,550± 380	11,190± 970
SERV-M (852Z).....	90-pct-Al_2O_3 brick..........	23,810±3,550	24,000±2,170
MONOFRAX K-3......	60-pct-Al_2O_3 chrome brick...	25,460±3,940	26,380±3,850
NUCON 60..........	Mag-chrome brick............	5,670± 900	4,570± 570
GUIDON............	...do......................	9,810±2,060	8,130± 790
GR-200............	...do......................	8,040±1,650	7,110± 440
DIBOND 50.........	...do......................	8,310±1,760	7,690±1,330
MONOFRAX E........	Chrome-mag brick............	24,940±3,840	20,730±2,550
REFRAX 20.........	Silicon carbide brick.......	23,360±7,740 ↔	Disintegrated

[1]95-pct confidence intervals shown. Significant difference at 99-pct confidence level is indicated by "↔".

[2]Fired in air at 980° C for 250 h.

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Brick surface
exposed to steam
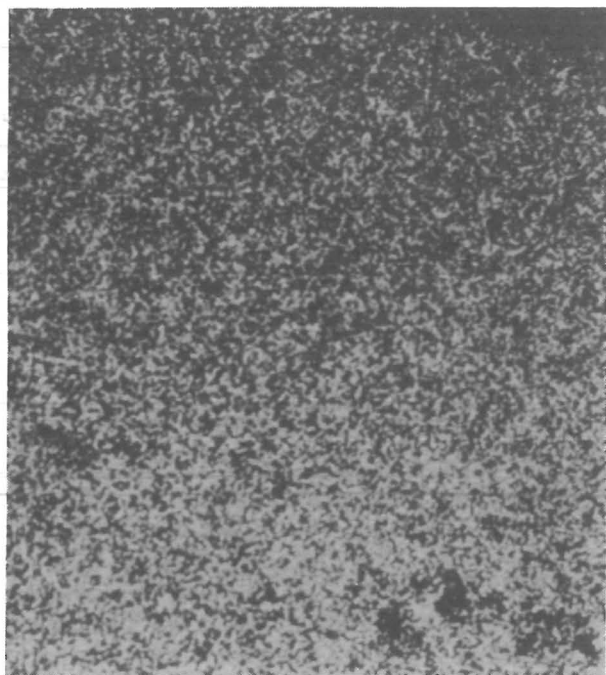
FIGURE 12. - Scanning electron micrograph of silica distribution in a 50-pct-silica brick after steam exposure. (X 200)

Scanning electron micrograph (SEM) examination of the fracture surfaces of samples of the CA-bonded concrete indicated that changes had occurred in the refractory microstructure at the cement-aggregate interface in both high- and intermediate-alumina castables. The leftmost column of photomicrographs in figure 13 is of the 95-pct-Al_2O_3 castable made from tabular alumina aggregate and high-purity CA cement. The marked grain growth of the tabular alumina aggregate could most likely be associated with the loss in strength of this refractory, since there was no change in the XRD mineralogy.

The SEM photographs in the middle column of figure 13 of the CA-bonded 55-pct-Al_2O_3 castable indicated that large gains in strength in this refractory following exposure to the steam-containing atmospheres corresponded with the development of a microstructure of interlocking grains in the bond phase. Energy-dispersive X-ray analysis spectra

identified the rod-shaped grains as predominantly aluminum and silicon (mullite), whereas the spherical grains were composed of aluminum, silicon, and calcium (anorthite). Although mullite was the major phase after all treatments, less CA_2 and cristobalite and more anorthite (CAS_2) were present in intermediate-alumina castable specimens exposed to steam-containing atmospheres than in air-fired specimens. Similar microstructural changes (not shown) were observed in intermediate-alumina castables with a low-purity CA-cement binder after the same treatment.

To determine whether the strength increases occurring in intermediate-alumina castables after exposure to high-pressure steam atmospheres were due to hydrothermal formation of anorthite or to hydrothermally induced microstructural changes occurring in the mullite present, a mixture of 75 pct calcined clay with 25 pct raw kaolin (containing <1 pct CaO) was formulated in the laboratory and exposed to high-pressure steam. Mullite crystal development (figure 13, rightmost column) and a fourfold increase in compressive strength were observed for the calcined clay-kaolin mixture following steam exposure. Table 12 lists comparative strength and XRD phase identification data for the 55-pct-Al_2O_3 castable and the calcined clay-kaolin mixture.

Even though the calcined clay-kaolin composition showed no formation of anorthite, as would be expected because of its low CaO content, there were a fourfold increase in strength and development of an interlocking grain structure. These results further support the contention that the higher strength of the intermediate-alumina refractory castables after exposures to high-pressure, steam-containing environments is due to the development of an interlocking network of rod-shaped mullite crystals.

Additional exposures of laboratory-formulated high-alumina castables in which intermediate-purity cement was substituted for high-purity cement were conducted. Strength tests conducted on

these specimens following 250-h exposures to the high-pressure, high-temperature steam atmosphere failed to show any improvement in strength in these compositions when compared to identical air-fired specimens.

Exposure to Steam at 1,000 psig and 815° C

The Exxon catalytic coal gasification (CCG) process represents a third-generation coal gasification scheme. An 815° C gasifier reactor temperature, typical of the reactor temperatures for this process, was used in screening candidate refractories. Table 13 presents comparative compressive strength data for several refractories after the 815° C steam exposure and after air firing for 250 h at 815° C. Based on compressive strength data, the 95-pct-Al_2O_3 CA-bonded castable was not significantly affected by steam at this low temperature, while in previous exposures to steam or steam-containing gas mixtures, at higher temperatures,

TABLE 12. – Strength data and mineralogical composition of intermediate Al_2O_3 castables heated at 980° C for 250 h in air or steam at 1,000 psig

Refractory	Compressive strength, psi		Mineralogy	
	Air, atm pressure	Steam, 1,000 psig	Air, atm pressure	Steam, 1,000 psig
Calcined clay and raw kaolin.	1,955	7,825	Mullite, cristobalite, rutile.	Mullite, cristobalite, tridymite, rutile.
CA-bonded 55-pct-Al_2O_3 dense castable.	3,355	11,330	Mullite, cristobalite, C_2AS, CA, CA_2.	Mullite, anorthite, cristobalite, Al_2O_3.

Air 980° C Atmospheric pressure 1,000 h

Steam 980° C 1,000 psig 1,000 h

95-pct-Al_2O_3 dense castable   55-pct-Al_2O_3 dense castable   75 pct calcined clay, 25 pct kaolin
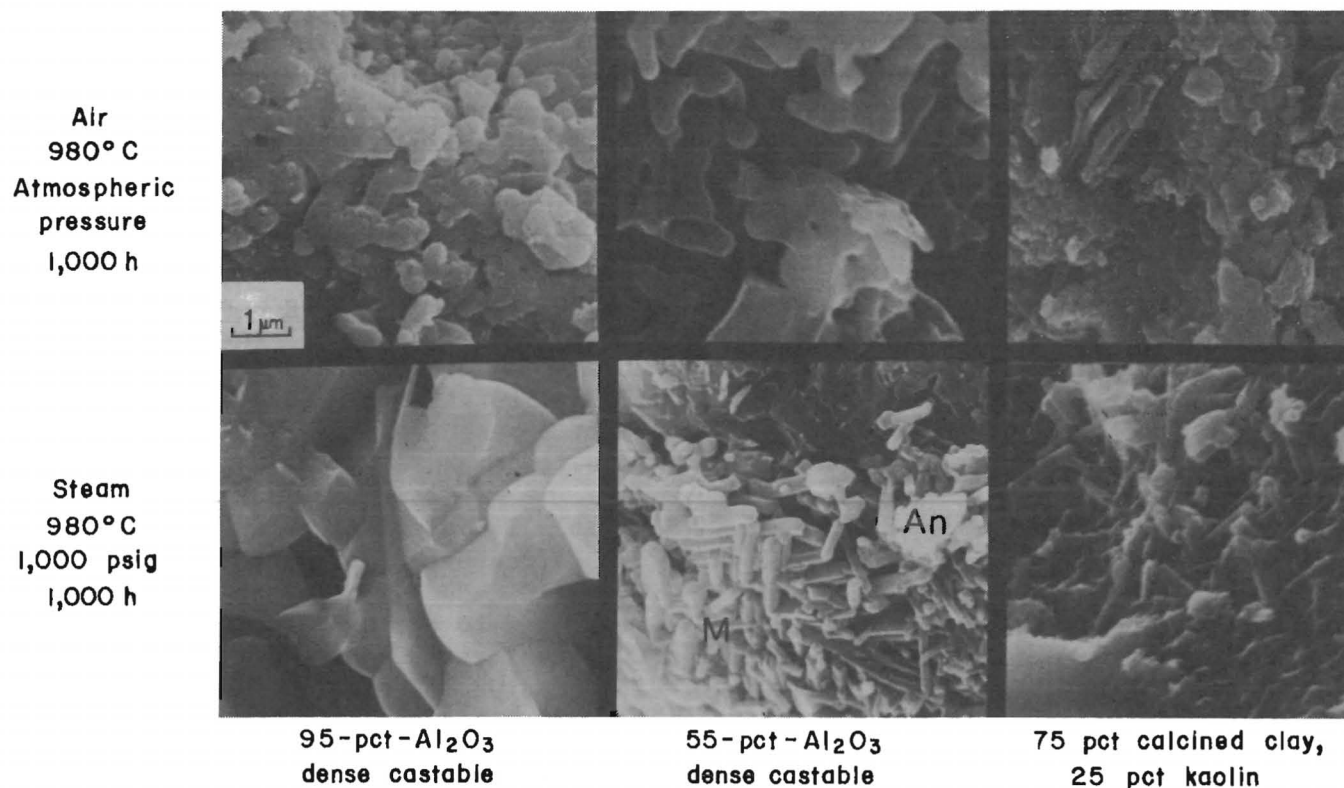
FIGURE 13. - Scanning electron micrographs of Al_2O_3 refractories exposed at 980° C to atmospheres and pressures indicated (M = mullite, An = anorthite).

TABLE 13. – Results of exposing refractories to steam at 815° C
and 1,000 psig for 250 h

Trade name	Classificaation	Compressive strength, psi[1]	
		Air fired[2]	Steam
CASTOLAST G.......	CA-bonded 95-pct-Al_2O_3 dense castable.	8,710±2,725	7,475± 360
LOABRADE..........	CA-bonded 55-pct-Al_2O_3 dense castable.	1,607± 270	←→ 5,660± 380
H.S. BRIKCAST B.F.	CA-bonded 50-pct-Al_2O_3 dense castable.	3,280± 290	←→ 11,550± 620
KAOCRETE D........	CA-bonded 45-pct-Al_2O_3 dense castable.	2,870±1,090	←→ 9,540± 545
LITECAST 75-28....	CA-bonded 50-pct-Al_2O_3 insulating castable.	1,865± 200	←→ 2,925± 390
CA-25.............	78-pct-Al_2O_3 CA cement.......	9,195±1,300	10,860±1,260
AA-22.............	Phosphate-bonded 90-pct-Al_2O_3 dense castable.	6,910±1,680	←→ 4,880± 400
BRIKRAM 90R.......	Phosphate-bonded 90-pct Al_2O_3 ramming mix.	14,940±4,680	12,795± 970
HW 23-75..........	Phosphate-bonded 60-pct Al_2O_3 ramming mix.	9,150±1,405	8,135±1,165
ARCO 90...........	90-pct-Al_2O_3 brick...........	24,780±4,035	24,325±2,540
KX-99.............	45-pct-Al_2O_3 brick...........	8,370±2,740	←→ 14,205±3,155

[1]95-pct confidence intervals shown. Significant difference at 99-pct confidence level is indicated by "←→".
[2]Fired in air at 815° C for 250 h.

significant strength losses were found. The lower alumina castables showed even greater increases in strength than in previous steam exposures. Low-alumina brick specimens also gained appreciable strength, while a high-alumina phosphate-bonded ramming mix lost a significant amount of its strength. The results from these steam exposures were in general agreement with results reported for steam-hydrogen atmospheres at 260° to 538° C (8).

Exposure to Steam and Carbon Monoxide-Steam Mixtures at 105 psig and 1,000° C

To evaluate candidate refractory liner materials for the ICGG-CoGas coal gasifier, exposure tests were conducted in pure steam and in two gas mixtures in which the CO-steam ratios were 3.5 and 7.0, at 1,000° C and 105 psig for 250 h. Characterization tests included bulk density, apparent porosity, dimensional change, MOR, and abrasion resistance.

The results of abrasion resistance and compressive strength determinations on six refractories are presented in table 14. With the exception of GREENKON 30, all the refractories either were unaffected by or showed physical property improvements after exposure to steam or CO-steam mixtures. As observed in previous tests, steam-containing environments improve the strength of low-alumina castables, and CO-containing environments appear to have no adverse effects on alumina-based refractories at lining-hotface temperatures.

Table 14 also presents MOR data of 19 refractories exposed for 250 h at 1,000° C and 105 psig to atmospheres of steam and to a gas mixture in which the CO-steam ratio was 3.5. Most of the intermediate-alumina dense castables showed statistically significant improvements in MOR after exposure. Two of the high-alumina dense concretes showed significant strength decreases.

TABLE 14. – Results of exposing refractories to steam and carbon monoxide-steam at 105 psig and 1,000° C for 250 h

Trade name	Classification	Abrasion loss, cm³				Compressive strength, psi				MOR, psi		
		Air fired[1]	H₂O	CO-H₂O, 3.5 ratio	CO-H₂O, 7.0 ratio	Air fired[1]	H₂O	CO-H₂O, 3.5 ratio	CO-H₂O, 7.C ratio	Air fired[1]	H₂O	CO-H₂O, 3.5 ratio[2]
GREENCAST-94.....	CA-bonded 95-pct-Al₂O₃ dense castable.	ND	ND	ND	ND	ND	ND	ND	ND	1,510	1,170	1,220
PLICAST L-2284...	...do...................	1.37	1.75	1.55	1.14	12,670	11,190	15,910	14,630	3,450	*1,670	3,350
GREENKON-30......	CA-bonded 85-pct-Al₂O₃ dense castable.	2.65	3.14	ND	3.12	6,410	5,650	ND	*3,270	1,670	*1,110	750
LO-ERODE.........	CA-bonded 60-pct-Al₂O₃ dense castable.	ND	ND	ND	ND	ND	ND	ND	ND	440	*1,040	*1,260
RESCO 17E........	CA-bonded 55-pct-Al₂O₃ dense castable.	5.89	*2.41	*3.88	*3.90	6,070	*12,180	*7,660	6,680	950	*2,680	2,810
HyMOR 3000.......	CA-bonded 50-pct-Al₂O₃ dense castable.	4.09	*3.62	4.35	*2.81	5,570	*7,710	ND	*6,630	1,110	1,270	1,300
BLAST FURNACE CASTABLE 122 N.	CA-bonded 50-pct-Al₂O₃ gunning mix.	ND	ND	ND	ND	ND	ND	ND	ND	270	*640	690
BLAST FURNACE GUN CASTABLE.	CA-bonded 45-pct-Al₂O₃ gunning mix.	ND	ND	ND	ND	ND	ND	ND	ND	1,150	1,590	1,350
KAOLITE-3300.....	CA-bonded 95-pct-Al₂O₃ insulating castable.	ND	ND	ND	ND	ND	ND	ND	ND	130	160	ND
KAST-O-LITE-30...	CA-bonded 60-pct-Al₂O₃ insulating castable.	ND	ND	ND	ND	ND	ND	ND	ND	190	*440	ND
GREENCAST 26-L...	...do...................	ND	ND	ND	ND	ND	ND	ND	ND	20	20	ND
LITECAST 75-28...	CA-bonded 50-pct-Al₂O₃ insulating castable.	ND	ND	ND	ND	ND	ND	ND	ND	400	540	ND
PLICAST LWI 20...	CA-bonded 40-pct-Al₂O₃ insulating castable.	ND	ND	ND	ND	ND	ND	ND	ND	100	120	ND
VSL-50...........	CA-bonded 30-pct-Al₂O₃ insulating castable.	ND	ND	ND	ND	ND	ND	ND	ND	40	110	ND
BRIKRAM 90R......	Phosphate-bonded 90-pct-Al₂O₃ ramming mix.	ND	ND	ND	ND	ND	ND	ND	ND	3,010	2,970	3,490
KAO-PHOS 93......	...do...................	ND	ND	ND	ND	ND	ND	ND	ND	1,680	1,870	1,850
LAVALOX X-8......	Phosphate-bonded 85-pct-Al₂O₃ chrome plastic.	.86	.83	.92	.82	9,050	11,230	8,250	10,990	5,710	5,920	ND
KRITAB..........	...do...................	ND	ND	ND	ND	ND	ND	ND	ND	3,330	*3,760	3,820
KRICOR...........	90-pct-Al₂O₃ brick......	2.14	2.35	1.98	1.82	6,040	*13,010	*13,380	*14,640	3,220	*3,890	3,690

ND Not determined.   [1]Fired in air at 1,000° C for 250 h.

[2]Too few specimens for statistical comparison, expect for GREENCAST-94, LO-ERODE, and KRITAB.

NOTE.--Askerisks indicate significant difference at 99-pct confidence level when compared with the air-fired companion specimens.

Comparing the effect of the different individual gases (H_2, CO, CO_2, and steam) at the temperatures of the lining hot face, steam and hydrogen appear to be the most active components in coal gasifier atmospheres, at least for the refractories included in these tests. CA-bonded intermediate-alumina castables in general showed significant increases in strength after exposure to steam and to a lesser degree to hydrogen. The largest increases were noted in the castables containing intermediate- and low-purity cements. The high-alumina castables showed a decrease in strength after exposure to steam and hydrogen. These results are in general agreement with those of Lang, Ballard, and Day (8-9).

GAS MIXTURES

Exposure to High-Btu Gas at 1,000 psig and 980° C

Identical specimens of each of the refractories listed in table 15 were exposed to high-Btu gas 1 (composition listed in table 5) for 160, 250, and 1,000 h. In all exposures the composition of the test gas exiting the pressure vessel was different from that of the gas entering the system: There were more H_2 and CO_2 and less steam, CH_4, and CO exiting the sample container than entering it.

When the sample container was opened at the completion of the 1,000-h exposure, white, powdery, and in some cases fibrous (0.5-mm length) deposits were found in the gas exit piping. Analysis by XRD showed these deposits to be amorphous. Energy-dispersive X-ray analysis identified silicon, aluminum, and calcium, in order of decreasing abundance.

Analysis of condensed water drained from the water separator in the reactive gas exit line indicated that the formation and transport of water-soluble compounds from the refractories by the gases leaving the sample container were minimal.[9]

With the exception of the silicon carbide specimens, there was no visible physical deterioration of the specimens after this exposure. The silicon carbide specimens were severely bloated and partially disintegrated, as shown in figure 14. Analysis by XRD showed that most of the SiC in the specimens had reacted to form SiO_2 (cristobalite). Only a slight reduction in P_2O_5 content of the phosphate-bonded ramming mix was detected after this exposure. Statistically significant reductions in strength were observed in the CA-bonded 95-pct-Al_2O_3 castable and in the phosphate-bonded 90-pct-Al_2O_3 castable. Significantly higher strengths after exposure to the gasifier atmosphere were measured for all three exposure times for the other CA-bonded refractory castables tested. Differences in bulk density between the air-fired and test-gas-exposed specimens were <2 pct in all cases, with the exception of the silicon carbide specimens. Table 16 shows the effect of the 1,000-h exposure on the mineralogies of the various samples.

SEM examination of fracture surfaces of samples exposed to the steam-containing high-Btu gas 1 atmosphere at 980° C for 1,000 h revealed changes in the refractory microstructure at the cement-aggregate interface in both high- and intermediate-alumina concrete. The high-alumina concrete, which lost strength when exposed to high-Btu gas 1, showed grain growth, while microstructural changes in the intermediate-alumina refractory, which showed large gains in strength, were characterized by the development of a structure of interlocking rod-shaped mullite grains. Similar

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[9]Dissolved solids concentration (g/L) in condensate: Ca 0.002, P 0.0002, Al 0.0004, Si 0.01. Distilled water was used as makeup to the steam generator.

TABLE 15. – Results of exposing refractories to high-Btu gas 1 at 980° C and 1,000 psig for 160, 250, and 1,000 h

Trade name	Classification	Compressive strength, psi[1]					
		160 h		250 h		1,000 h	
		Air fired[2]	High-Btu gas 1	Air fired[2]	High-Btu gas 1	Air fired[2]	High-Btu gas 1
CASTOLAST G[3].	CA-bonded 95-pct-Al$_2$O$_3$ dense castable.	3,480± 590 ↔	2,520± 80	ND	ND	3,660± 540 ↔	2,460± 250
Do.[4]	...do...............	ND	ND	9,810± 1,590 ↔	6,880±1,305	9,710±1,710 ↔	7,650±1,240
LOABRADE.....	CA-bonded 55-pct-Al$_2$O$_3$ dense castable.	1,500± 190 ↔	2,360± 140	1,920± 275 ↔	4,545± 715	1,530± 80 ↔	3,740± 880
H.S. BRICK-CAST B.F.	CA-bonded 50-pct-Al$_2$O$_3$ dense castable.	4,440± 200 ↔	10,860±1,030	3,090± 270 ↔	10,960±1,440	3,340± 260 ↔	12,740±1,560
KAOCRETE D...	CA-bonded 45-pct-Al$_2$O$_3$ dense castable.	ND	ND	2,285± 300 ↔	7,285± 500	ND	ND
LITECAST 75-28.	CA-bonded 50-pct-Al$_2$O$_3$ insulating castable.	1,880± 270 ↔	2,710± 170	1,280± 125 ↔	3,130± 255	1,010± 110 ↔	3,050± 430
CA-25........	78-pct-Al$_2$O$_3$ CA cement.	9,420±3,130	9,430±1,280	10,355± 810	9,390±1,465	10,960±1,710	9,950±2,910
AA-22........	Phosphate-bonded 90-pct-Al$_2$O$_3$ dense castable.	6,060± 860	5,180±1,000	8,105± 625 ↔	5,045± 320	6,590± 790 ↔	3,840± 560
BRIKRAM 90R..	Phosphate-bonded 90-pct-Al$_2$O$_3$ ramming mix.	19,080±4,390	15,940±4,170	19,145± 1,980 ↔	12,685±2,095	15,860±2,090	14,200±5,380
HW 23-75.....	Phosphate-bonded 60-pct-Al$_2$O$_3$ ramming mix.	ND	ND	13,150± 3,035	11,430± 780	ND	ND
99 AD........	99-pct-Al$_2$O$_3$ brick...	7,250±1,820 ↔	10,280±1,480	ND	ND	8,160±2,500	8,510±1,780
ARCO 90......	90-pct-Al$_2$O$_3$ brick...	25,530±3,820	27,340±6,410	18,115±12,340	20,410±1,905	24,150±1,770	25,530±4,150
UFALA TI.....	60-pct-Al$_2$O$_3$ brick...	9,480±2,660	11,480±2,080	ND	ND	16,140±3,380	15,860±4,460
KX-99........	45-pct-Al$_2$O$_3$ brick...	10,960±1,890 ↔	13,070±5,560	12,715± 4,810	13,880±1,895	10,710±4,320	14,110±2,140
REFRAX 20....	Silicon carbide brick	ND	ND	ND	ND	23,360±7,740 ↔	Disintegrated

ND Not determined.

[1] 95-pct confidence intervals shown. Significant difference at 99-pct confidence level is indicated by "↔".
[2] Fired in air at 980° C.
[3] Original group of prepared samples.
[4] Samples prepared from new shipment of castable.

TABLE 16. – Effect of high-Btu gas 1 exposure at 980° C and 1,000 psig
for 1,000 h on refractory mineralogy

| Trade name	Classification	Difference in amount of phase detected in exposed samples relative to air-fired samples
CASTOLAST G..	CA-bonded 95-pct-Al_2O_3 dense castable.	Less CA_2.
LOABRADE.....	CA-bonded 55-pct-Al_2O_3 dense castable.	Much less CA_2.
H.S. BRIKCAST B.F.	CA-bonded 50-pct-Al_2O_3 dense castable.	Much less CA_2 and C_2AS, more anorthite.
LITECAST 75-28.	CA-bonded 50-pct-Al_2O_3 insulating castable.	Much less kyanite, less quartz, much less tridymite.
CA-25........	78-pct-Al_2O_3 CA cement.	No difference.
AA-22........	Phosphate-bonded 90-pct-Al_2O_3 dense castable.	Do.
BRIKRAM 90R..	Phosphate-bonded 90-pct-Al_2O_3 ramming mix.	Do.
99 AD........	99-pct-Al_2O_3 brick...........	Much less β-$NaAl_{11}O_{17}$.
ARCO 90......	90-pct-Al_2O_3 brick...........	No difference.
UFALA TI.....	60-pct-Al_2O_3 brick...........	Much more tridymite.
KX-99........	45-pct-Al_2O_3 brick...........	Do.
REFRAX 20....	Silicon carbide brick........	Much less SiC, much more cristobalite.
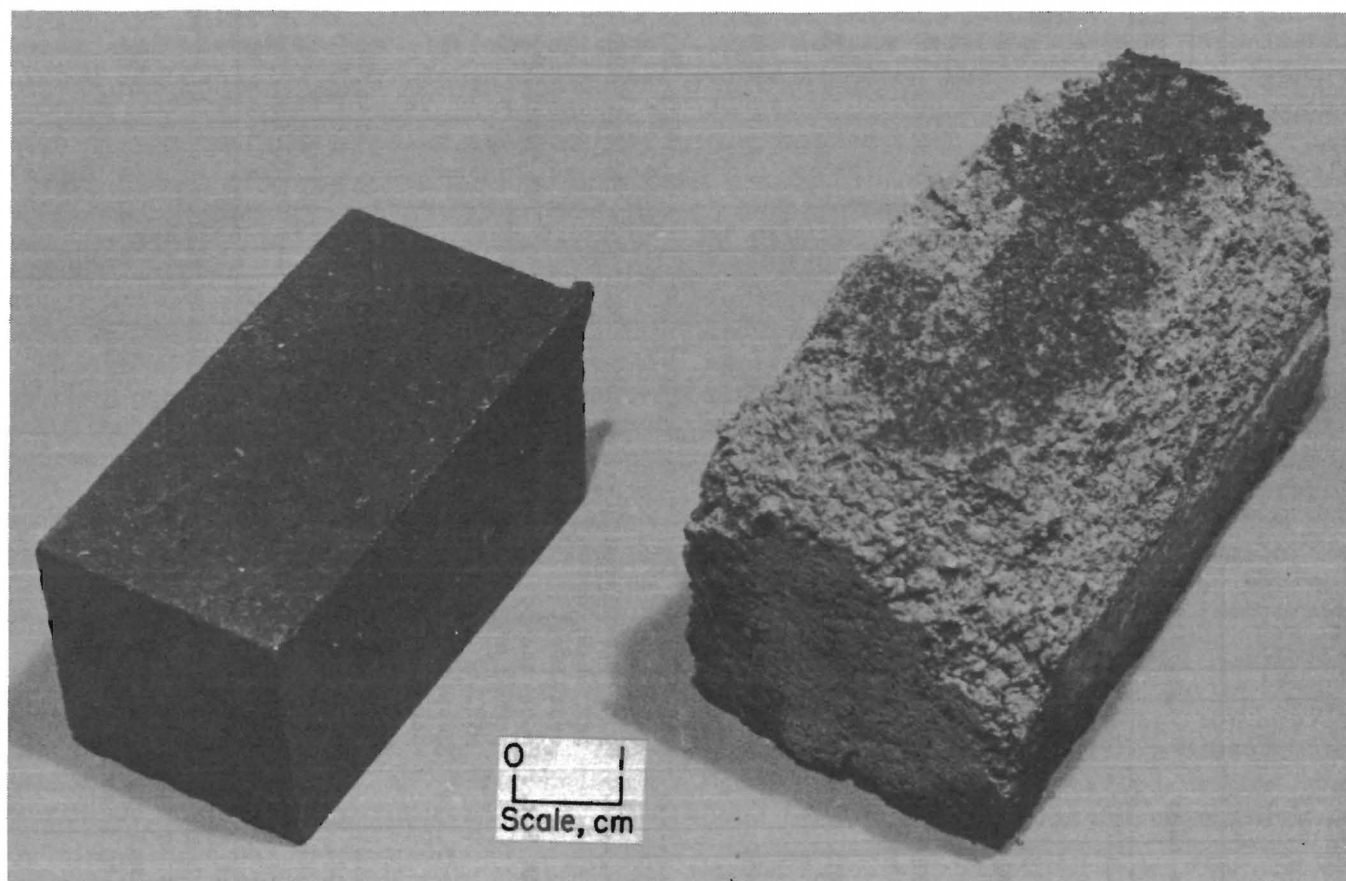
FIGURE 14. - Silicate-bonded silicon carbide refractory before and after high-Btu gas 1 exposure at 980° C and 1,000 psig for 1,000 h.

observations were noted in refractories exposed to steam atmospheres, as previously shown in figure 13.

A comparison of the effects of 160-, 250-, and 1,000-h exposures to the gasifier atmosphere on refractory strength can be made from the data in table 15. The data indicate that for the CA-bonded 95-pct-Al_2O_3 dense castable, losses in strength occurred rapidly but tended to level off after 160 h. Observed strength increases in the intermediate-alumina refractory castables also occurred rapidly and tended to level off after 160 h. The phosphate-bonded 90-pct-Al_2O_3 castable refractory continued to lose strength over the entire exposure period, while the strength of the phosphate-bonded 90-pct-Al_2O_3 ramming mix appeared to level off after 160 h. As shown in table 16, less CA_2 was found in the dense CA-bonded refractory concretes after the 1,000-h exposure to the gasifier atmosphere than after firing in air.

A 250-h exposure test was conducted to evaluate the performance of additional refractory compositions, listed in table 17, some of which were being considered at the time (10) for use in a slagging gasifier operated at 980° C and 1,000 psig with a gas composition similar to the high-Btu gas 2 atmosphere.

Statistical analyses of the compressive strength indicated that the low-purity CA-bonded 40-pct-Al_2O_3 insulating castable was not affected by the exposure. The low- and high-purity cement-bonded 45- and 50-pct-Al_2O_3 concrete gained significant strength, as did other refractory castables of similar compositions in earlier tests. The phosphate-bonded alumina chrome ramming mix also showed a significant strength increase following exposure to the high-Btu gas 2 mixture. The chrome ore plastic showed a decrease in strength, and the silicon-nitride-bonded silicon carbide brick was partially disintegrated.

TABLE 17. – Results of exposing refractories to high-Btu gas 2
at 980° C and 1,000 psig for 250 h

Trade name	Classification	Compressive strength, psi[1]	
		Air fired[2]	High-Btu gas 2
Q-GUN 30-50........	CA-bonded 50-pct-Al_2O_3 gunning mix.	2,270± 110 ↔	4,620± 560
Q-CRETE 25 HS......	CA-bonded 45-pct-Al_2O_3 dense castable.	3,090± 330 ↔	7,200±1,280
PLASTIC INSULCRETE.	CA-bonded 40-pct-Al_2O_3 insulating castable.	390± 50	440± 30
SHAMROCK 888.......	Phosphate-bonded 85-pct-Al_2O_3 ramming mix.	11,010±1,530 ↔	14,840±1,370
KEMRAM.............	Phosphate-bonded 40-pct-Cr_2O_3 ramming mix.	15,250± 870 ↔	9,180±1,260
RUBY..............	90-pct-Al_2O_3 chrome brick.	12,470±1,030	11,810±1,360
SERV-M (852Z)......	90-pct-Al_2O_3 brick....	20,470±3,630	22,280±2,190
MONOFRAX K-3.......	60-pct-Al_2O_3 chrome brick.	24,540±5,300	26,800±2,750
GUIDON.............	Mag-chrome brick......	8,680±1,240	7,270±1,350
MONOFRAX E.........	Chrome-mag brick......	20,140±2,910	22,820±4,400
REFRAX 20..........	Silicon carbide brick.	20,570±3,420 ↔	Disintegrated

[1]95-pct confidence intervals shown. Significant difference at 99-pct confidence level is indicated by "↔".
[2]Fired in air at 980° C for 250 h.

X-ray diffraction analyses of the re-fractories following exposure to the high-Btu gasifier atmosphere showed very little change in mineralogy except for the two refractories suffering strength loss. Iron oxide in the phosphate-bonded 40-pct-Cr_2O_3 ramming mix combined with Cr_2O_3 to form chromite ($FeCr_2O_4$) as a result of the exposure. In the case of the SiC refractory, cristobalite and quartz had developed.

Hot MOR Evaluation

To determine the effect of the gasifier environment on the high-temperature strength properties of the intermediate-alumina castables, hot MOR measurements were made on 1- by 1- by 6-in specimens of a 50- and a 55-pct-Al_2O_3 castable. Strengths were measured at 600°, 800°, 1,000°, and 1,200° C on samples after they were exposed to the high-Btu gas 1 atmosphere at 980° C and 1,000 psi for 250 h. These data were compared with data taken on identical specimens fired in air at 980° C and 1 atm for the same length of time.

As shown in figure 15, exposure to the high-Btu gas significantly increased hot MOR values of the 50-pct-Al_2O_3 dense castable, which contained a calcined fireclay aggregate and an intermediate-purity CA cement. This gain in hot strength was maintained at all test temperatures. The hot MOR values, as shown in figure 16, for air-fired and mixed gas-exposed specimens of the 55-pct-Al_2O_3 castable (which contained a calcined fireclay aggregate and a high-purity CA cement) were not significantly different.

Castables That Contain Metal Fibers

Table 18 lists compressive strength results on CA-bonded 95- and 55-pct-Al_2O_3 dense castables that contained metal fibers and were exposed to the high-Btu gas at 980° C and 1,000 psig for 250 h. The compressive strengths of these refractories were affected in the same way by mixed gas exposure as were the strength of the same compositions that did not contain fibers. The lower strength of CASTOLAST G specimens containing fiber reinforcement could have been expected from the findings of other investigators (11). In general, the refractory showed no degradation following the mixed gas exposure, but some fiber degradation was apparent in cases where the fibers extended to the exposed surface of the refractory. Metal fibers within the sample, however, appeared unaffected.

TABLE 18. — Results of exposing CA-bonded Al_2O_3 castables containing stainless steel fibers to high-Btu gas 2 at 980° C and 1,000 psig for 250 h

Refractory	Compressive strength, psi[1]	
	Air fired[2]	High-Btu gas 2
CASTOLAST G:		
No fiber addition..............	9,810 ←|→	6,880
Plus 430 SS fiber.............	7,680 ←|→	6,090
Plus 446 SS fiber.............	8,385 ←|→	6,925
Plus coated 446 SS fiber......	7,540	6,940
Plus 310 SS fiber.............	7,280 ←|→	5,735
H.S. BRIKCAST B.F.:		
No fiber addition..............	3,090 ←|→	10,960
Plus 430 SS fiber.............	3,025 ←|→	10,625
Plus 446 SS fiber.............	4,130 ←|→	11,630
Plus coated 446 SS fiber......	4,130 ←|→	12,155
Plus 310 SS fiber.............	4,150 ←|→	12,245

[1]Significant difference at 99-pct confidence level is indicated by "↔".
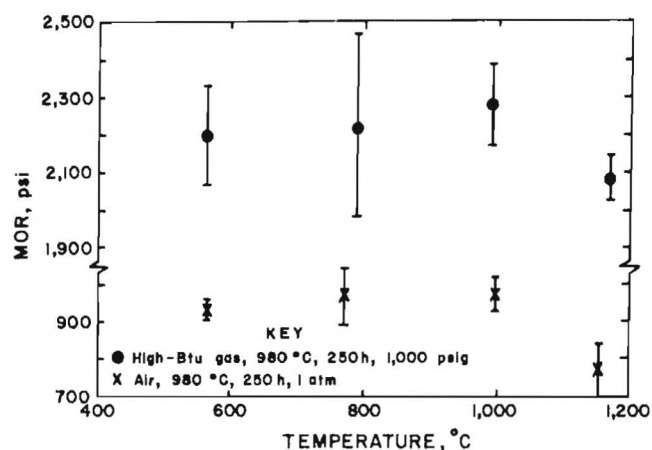
[2]Fired in air at 980° C for 250 h.

FIGURE 15. - Hot MOR data of 50-pct-Al$_2$O$_3$ refractory dense castable containing intermediate-purity CA cement.

FIGURE 16. - Hot MOR data of 55-pct-Al$_2$O$_3$ refractory dense castable containing high-purity CA cement.

Silica Volatilization Evaluation

There had been little visual evidence of silica migration at temperatures of 980° C and below in prior exposures in which high-silica refractories were present. Significant silica movement was evident when specimens were exposed to steam at 1,100° C and 1,000 psig in the high-temperature exposures completed early in the test program.

To study possible silica loss through volatilization from high-silica low-alumina refractories, a 250-h exposure of both a high-purity CA-bonded 55-pct-Al$_2$O$_3$ castable and a refractory fiber (KAOWOOL) to a high-Btu gas 2 atmosphere at 1,000 psig and 980° C was conducted. The data in table 19 show that silica losses from the castable specimens in the low-gas-velocity section of the sample container (fig. 8) were negligible under these conditions. Slight losses may have occurred in the crushed material subjected to higher gas velocities in the standpipe. The compressive strength of the exposed bars increased similarly to that of low-alumina castables in previous exposures to steam-containing atmospheres. The refractory fiber insulation specimens were found to contain 50.8 pct SiO$_2$ after 250-h exposure, compared with 51.4 pct prior to exposure. Temperatures of 980° C and below are probably too low for much silica transport to occur.

TABLE 19. - Results of exposing 55-pct-Al$_2$O$_3$ castable and a refractory insulating fiber to high-Btu gas 2 at 980° C and 1,000 psig for 50 to 250 h

Time, h	Bars, sample container	SiO$_2$ content, wt pct					Refractory fiber	Compressive strength, psi,[1] of 1- by 1- by 2-in bars	
		20-mesh material							
		Sample container	Standpipe				Air fired	High-Btu gas 2
			Inlet	Middle	Exit				
0[2].....	36.3	36.3	36.3	36.3	36.3	51.4	3,180±300	ND
50.....	36.6	37.9	ND	ND	ND	ND	2,925±240	4,950±660
100....	36.6	37.1	34.0	35.3	34.9	ND	2,450±180	4,100±420
150....	35.9	37.1	ND	ND	ND	50.5	2,510±280	5,750±560
200....	36.3	37.2	ND	ND	ND	ND	2,320±160	3,750±360
250....	36.5	36.8	ND	ND	ND	50.8	2,080±160	5,970±440

ND Not determined.
[1]95-pct confidence intervals shown.
[2]Prefired in air at 980° C for 24 h.

Exposure to High-Btu Gas at 1,000 psig and 760° C

Table 20 compares compressive strength data for refractory specimens exposed to high-Btu gas 2 at 760° C with data for identical specimens fired in air for 250 h. Significant increases in strength after exposure to the gas mixture were observed in intermediate-alumina CA-bonded castables and brick. The 90-pct-Al_2O_3 phosphate-bonded castable had a statistically significant strength loss. A loss in strength was also observed for the CA-bonded high-alumina castable specimens, but it was not statistically significant at the 99-pct confidence level.

Silicon carbide brick specimens (direct-, silicate-, and oxynitride-bonded specimens) were also included in the 760° C high-Btu gas 2 exposure. Some specimens of each type of SiC brick were prefired in air at 1,500° C to produce a glassy coating prior to exposure to act as a barrier to gaseous attack. As shown in figure 17, following the high-Btu exposure, all SiC brick specimens were bloated. The brick specimens without the glassy coating were bloated to a greater extent and more often cracked than the SiC brick with the glassy coating.

In general, the same trends in refractory property changes were observed after the 760° C exposure that were detected after exposure to the same gas composition at 980° C for 250 h.

Exposure of the phosphate-bonded high-alumina castable to high-Btu gas environments resulted in lower strengths relative to the air-fired specimens at 760° C, as was also the case at 980° C. The intermediate-alumina phosphate-bonded refractory was not significantly affected by exposure to high-Btu gas 2 at 760° C. Even at 980° C there was less strength loss, relative to the air-fired specimens, in the intermediate-alumina phosphate-bonded castable than in the high-alumina phosphate-bonded castable.

TABLE 20. — Results of exposing refractories to high-Btu gas 2 at 760° C and 1,000 psig for 250 h

Trade name	Classification	Compressive strength, psi[1]	
		Air fired[2]	High-Btu gas 2
CASTOLAST G........	CA-bonded 95-pct-Al_2O_3 dense castable.	8,710±2,725	7,290±1,670
LOABRADE..........	CA-bonded 55-pct-Al_2O_3 dense castable.	1,607± 270 ↔	5,280± 415
H.S. BRIKCAST B.F..	CA-bonded 50-pct-Al_2O_3 dense castable.	3,280± 290 ↔	8,570±2,010
KAOCRETE D........	CA-bonded 45-pct-Al_2O_3 dense castable.	2,870±1,090 ↔	7,940± 615
LITECAST 75-28.....	CA-bonded 50-pct-Al_2O_3 insulating castable.	1,865± 200 ↔	2,475± 460
CA-25..............	78-pct-Al_2O_3 CA cement.	9,195±1,300	8,780±2,040
AA-22..............	Phosphate-bonded 90-pct-Al_2O_3 dense castable.	6,910±1,680 ↔	5,025± 575
BRIKRAM 90R........	Phosphate-bonded 90-pct-Al_2O_3 ramming mix.	14,940±4,680	15,420±2,765
HW 23-75..........	Phosphate-bonded 60-pct-Al_2O_3 dense castable.	9,150±1,405	8,115±1,735
ARCO 90...........	90-pct-Al_2O_3 brick......	24,780±4,035	20,470±5,670
KX-99.............	45-pct-Al_2O_3 brick......	8,370±2,740 ↔	14,265±6,160

[1]95-pct confidence intervals shown. Significant difference at 99-pct confidence level is indicated by "↔".
[2]Fired in air at 760° C for 250 h.
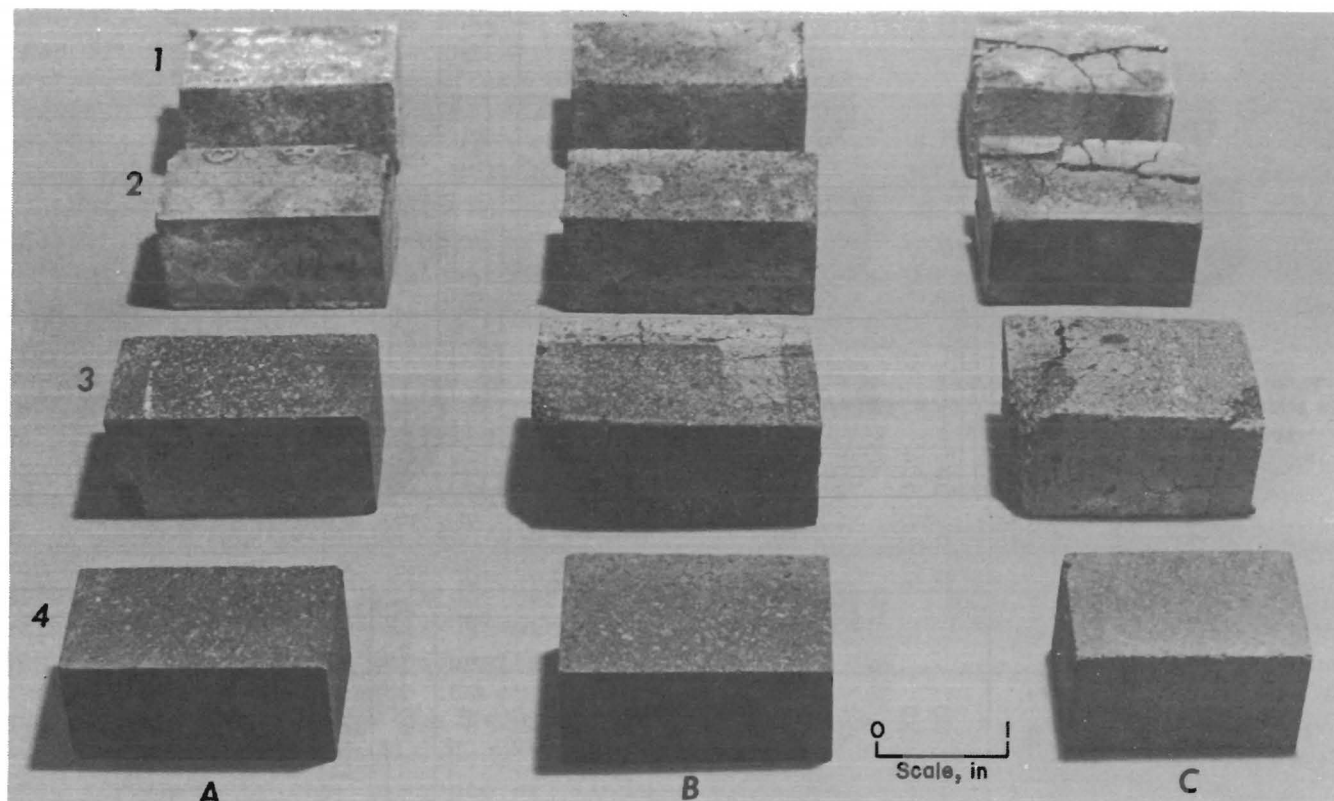
FIGURE 17. - Silicon carbide refractories exposed to high-Btu gas mixture. (Rows 1 and 2, specimens prefired to 1,500° C and exposed to gas mixture; row 3, specimens exposed to gas mixture but not prefired; row 4, specimens as received. Columns *A, B,* and *C* are silicate-, oxynitride-, and direct-bonded specimens, respectively.)

Exposure to High-Btu Gas at 1,000 psig and 500° C

Exposure of selected refractories to high-Btu gas at lower temperatures was conducted to gauge the effect of the high-Btu environment on interior portions of the gasifier reactor vessel lining. Previous exposures at 760° to 1,100° C had shown steam and hydrogen to be relatively aggressive, but few if any effects related to CO attack were observed.

Visual inspection of several of the refractories after a 58-h exposure to high-Btu gas 2 at 500° C indicated that, with the exception of the specimens containing stainless steel fiber reinforcement, this environment had little effect on the refractory concretes.

A group of insulating and dense-alumina refractory concretes was subsequently exposed at 500° C for 1,000 h to each of

the three high-Btu gas 1, 2, and 3 environments. The results from these exposures are summarized in table 21. To determine the effect of iron on the performance of these castables, 0.1 wt pct iron powder was added to some of the dense, high-alumina castable refractory specimens, and rust was added to one surface of some of the three insulating castables during sample preparation.

With regard to the dense castables, as had been reported in earlier tests in atmospheres similar to gases 1 (H_2S and NH_3 present), and 2 (no H_2S or NH_3 present) at higher temperatures (700° to 1,100° C), the intermediate-alumina concretes showed improvement in strength after exposure when compared to air-fired specimens. Likewise, as in earlier exposures, the high-alumina material showed a decrease in strength and abrasion resistance relative to air-fired samples. The results in table 21 show that, in

TABLE 21. – Results of exposing refractories to three different high-Btu gases[1] at 500° C and 1,000 psig for 1,000 h

Trade name	Classification	Abrasion resistance, volume refractory lost, cm^3				Compressive strength, psi			
		Air fired[2]	Gas 1	Gas 2	Gas 3	Air fired[2]	Gas 1	Gas 2	Gas 3
PLICAST LWI BUBBLE CAST.	CA-bonded 95-pct-Al_2O_3 insulating castable.	ND	ND	ND	ND	547← → 353		360	341
Do............	CA-bonded 95-pct-Al_2O_3 insulating castable plus rust.	ND	ND	ND	ND	534	393	418	314
PLICAST LWI-28..	CA-bonded 55-pct-Al_2O_3 insulating castable.	ND	ND	ND	ND	1,026	1,258←→1,688←→1,157		
Do............	CA-bonded 55-pct-Al_2O_3 insulating castable plus rust.	ND	ND	ND	ND	1,069←→1,508←→1,195			1,272
PLICAST LWI-20..	CA-bonded 40-pct-Al_2O_3 insulating castable.	ND	ND	ND	ND	1,090←→1,706		1,521	1,499
Do............	CA-bonded 40-pct-Al_2O_3 insulating castable plus rust.	ND	ND	ND	ND	814←→1,270		1,582←→ 940	
Laboratory mix..	CA-bonded 50-pct-Al_2O_3 dense castable.	1.09	1.29	1.34	1.51	6,970	7,993	9,283	10,135
Do............	CA-bonded 90-pct-Al_2O_3 dense castable.	1.30←→9.59←→ 4.42←→10.28				5,510←→2,268		2,306	1,840
Do............	CA-bonded 90-pct-Al_2O_3 plus 0.1 pct Fe.	1.26←→6.56←→16.39←→7.70				5,781←→2,771←→1,120←→2,515			

ND Not determined.
[1]Gas compositions are given in table 5.
[2]Fired in air at 500° C for 1,000 h.

NOTE.--Significant difference at 99-pct confidence level is indicated by "↔". (Long arrows indicate significant differences between the entries at the opposite ends of the arrow.)

general, the presence or absence of CO (gas 3) or H_2S and NH_3 (gas 2) in the mixture had little or no effect on compressive strength or abrasion resistance of the dense refractories, with the possible exception of the 90-pct-Al_2O_3 dense castable to which 0.1 pct Fe had been added. The strength and abrasion resistance of this dense castable seemed to be adversely affected by the presence of CO unless H_2S and NH_3 were present.

As with the dense castables, the lower alumina insulating materials became stronger, relative to air-fired specimens, after exposure to gases 1, 2, and 3, while the high-alumina castable became weaker. None of the insulating castables were tested for abrasion loss. The strengths of the 40- and 95-pct-Al_2O_3 insulating materials were unaffected by the presence or absence of CO or NH_3 and H_2S in the gas mixture. The 55-pct-Al_2O_3 castable seemed to have actually been made stronger by the presence of CO in the gas mixture. Additions of rust (iron oxide) to one surface of samples prior to casting appeared to produce no trend in strength changes. As shown in figure 18, surface popouts were observed on these specimens after exposure to the gas mixture containing CO but not H_2S and NH_3 (gas 2). No visual changes in surface appearance were observed in any of the specimens exposed to gases that did not contain CO (gas 3) or that contained CO, H_2S, and NH_3 (gas 1), as shown in figures 19 and 20. Jayatilleke, Martin, and Brown ([12]) also studied CO attack on refractory concretes to which iron (as Fe and Fe_2O_3) had been added. They investigated $CO-H_2O$, $CO-H_2$, and $CO-H_2O-H_2S$ atmospheres. They stated that damage occurred in all atmospheres except $CO-H_2S$. The exposures were run in a static system at 1,000 psig, 500° C, and for 50 h.

Exposure to Alkali-Containing High-Btu Gas

High-Btu Gas Environment Containing Potassium and Sodium

Two exposures were made at 980° C and 1,000 psig. In the first exposure (200
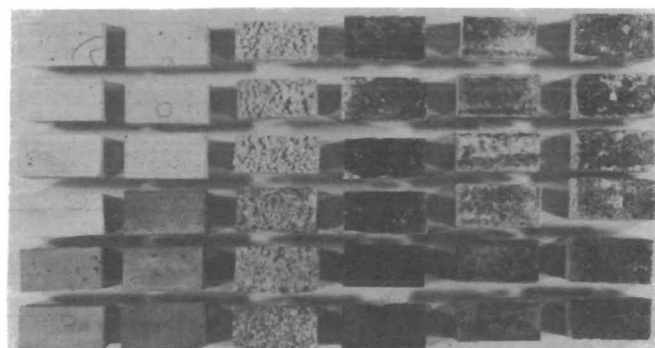
50 pct   55 pct   95 pct
Al_2O_3 insulating castables

50 pct   55 pct   95 pct
Al_2O_3 insulating castables with Fe_2O_3 particle rubbed onto surface
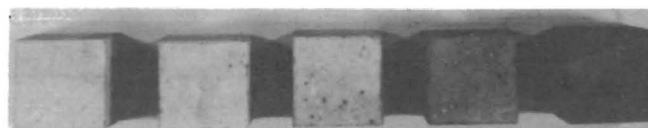
50-pct-Al_2O_3 dense castable
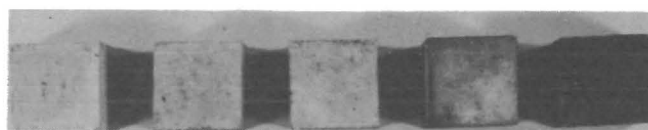
90-pct-Al_2O_3 dense castable

90-pct-Al_2O_3 dense castable with 0.1 pct Fe addition

0   2
Scale, in

FIGURE 18. - Refractory castables exposed to high-Btu gas 2 for 1,000 h at 500° C and 1,000 psig.

h), the sample container was loaded with 1- by 1- by 2-in bars for cold compressive strength testing. In the second exposure (250 h), 1- by 1- by 7-in bars for hot MOR testing were placed in the sample container. During the exposure of the specimens for compressive strength tests, listed in table 22, water condensed from the gas stream exiting the sample container was continuously analyzed for sodium and potassium. Analyses early in the exposure period showed that the water contained 1.5 ppm K_2O and 2.3 ppm Na_2O. By 125 h, these values had dropped to 0.2

50 pct   55 pct   95 pct   50 pct   55 pct   95 pct
Al₂O₃ insulating castables   Al₂O₃ insulating castables with
                                       Fe₂O₃ particle rubbed
                                          onto surface

50-pct-Al₂O₃ dense castable

90-pct-Al₂O₃ dense castable

90-pct-Al₂O₃ dense castable with O.I pct Fe addition
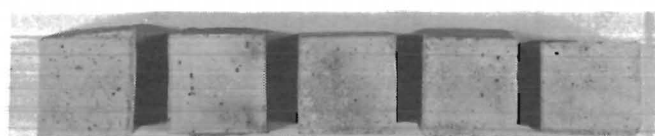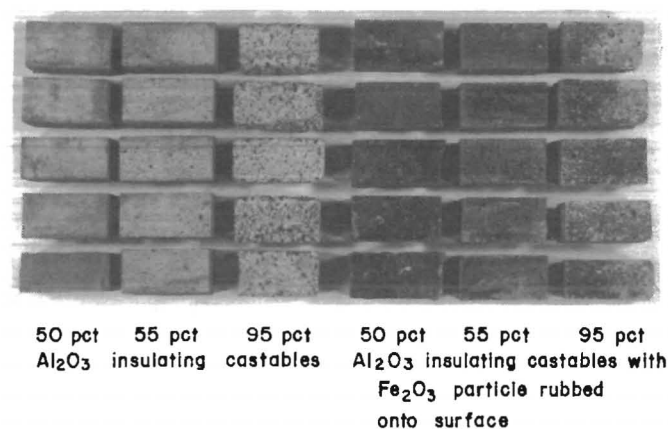
0   2
Scale, in

FIGURE 19. - Refractory castables exposed to high-Btu gas 3 for 1,000 h at 500° C and 1,000 psig.

50 pct   55 pct   95 pct   50 pct   55 pct   95 pct
Al₂O₃ insulating castables   Al₂O₃ insulating castables with
                                       Fe₂O₃ particle rubbed
                                          onto surface

50-pct-Al₂O₃ dense castable

90-pct-Al₂O₃ dense castable

90-pct-Al₂O₃ dense castable with O.I pct Fe addition

0   2
Scale, in

FIGURE 20. - Refractory castables exposed to high-Btu gas 1 for 1,000 h at 500° C and 1,000 psig.
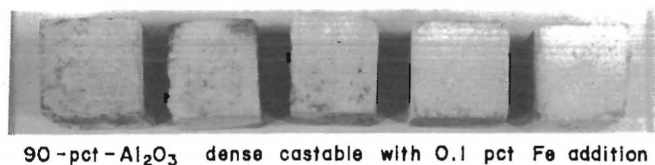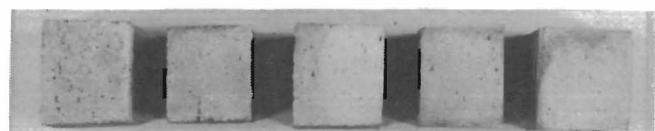
ppm K_2O and 0.35 ppm Na_2O. After 125 h, the exposure was interrupted to be certain that alkali was still present in the platinum crucibles. After opening the sample container, some specimens near the platinum crucibles showed signs of bloating and deterioration, but this appeared to be due to liquid alkali spattering from the crucibles rather than to vapor phase transport of alkali. Chemical analysis of the contents of the crucible showed the K_2O–Na_2O weight ratio had been reduced. The amount of alkali present in each crucible was found to have been reduced by approximately 50 pct.

Additional alkali was added to the platinum crucibles before proceeding with the exposure. The exposure was then restarted, but at 200 h total exposure time, sample container leaks forced termination of the exposure. When the sample container was opened, corrosion of the 310 stainless steel container walls was noted. Figure 21 shows the interior of the sample container and inlet gas standpipe after some specimens had been removed.

TABLE 22. – Potassium and sodium contents of refractories exposed to high-Btu gas 1 at 980° C and 1,000 psig for 200 h, weight percent

Treatment	CASTOLAST G		LOABRADE		H.S. BRIKCAST B.F.	
	K_2O	Na_2O	K_2O	Na_2O	K_2O	Na_2O
High-Btu gas, no alkalis...............	0.001	0.18	0.54	0.28	0.12	0.06
Alkali-containing high-Btu gas..........	.24	.33	1.4	.51	.82	.3
Soaked in alkali solution and dried:						
Fired in air.........................	1.3	1.3	2.9	1.9	2.4	1.5
Exposed to alkali-containing high-						
Btu gas.............................	1.3	1.4	3.5	2	3.3	2
	KAOCRETE D		AA-22		BRIKRAM 90R	
	K_2O	Na_2O	K_2O	Na_2O	K_2O	Na_2O
High-Btu gas, no alkalis...............	0.26	0.04	0.001	0.07	0.02	0.15
Alkali-containing high-Btu gas..........	1.8	.52	.7	.33	1.3	.53
Soaked in alkali solution and dried:						
Fired in air.........................	2.9	1.8	1.5	1.1	1.1	.8
Exposed to alkali-containing high-						
Btu gas.............................	3.5	2	2.4	1.1	1.4	.76

FIGURE 21. - Sample container following alkali-containing high-Btu gas 2 exposure at 980° C and 1,000 psig.
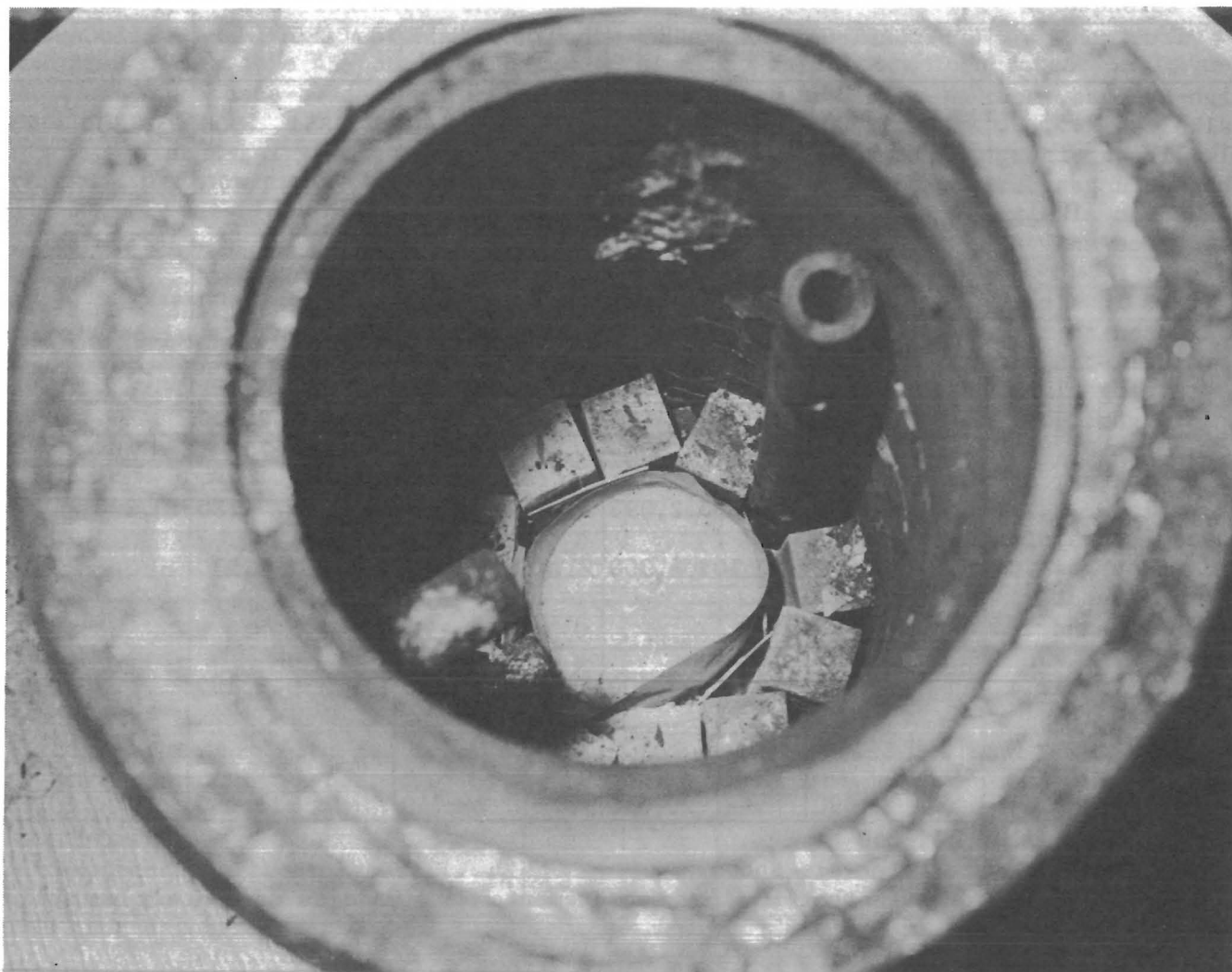
Specimens that, on the basis of visual examination, had not come into contact with molten alkali from the crucibles were submitted for chemical analysis. The K_2O and Na_2O analyses of some of the exposed specimens (table 22), show an increase in alkali content when compared with air-fired samples. This provided convincing evidence that alkali vapors were present in high concentration in the sample container. In addition, the alkali contents of specimens soaked in aqueous alkali solution and then air-fired were lower than the alkali contents of soaked specimens exposed to the alkali-containing gas mixture.

Table 23 presents cold compressive strength data for the specimens after exposure to the high-Btu gas 1 atmosphere with or without alkalis present at 980° C and 1,000 psig for 200 h. The specimens showing evidence of contact with molten alkali from the crucible (spattering) were not tested. Cold crushing strength values in the first two lines in table 23, which are for specimens not soaked in alkali prior to exposure, show little evidence that the presence of alkali vapor has a deleterious effect on cold crushing strength of the refractories tested, with the possible exception of AA-22. Unfortunately in the cases of

TABLE 23. — Compressive strengths of refractories exposed to potassium and sodium containing high-Btu gas 1 at 980° C and 1,000 psig for 200 h, pounds per square inch

Treatment	CASTOLAST G	LOABRADE	H.S. BRIKCAST B.F.	KAOCRETE D	LITECAST 75-28
High-Btu gas, no alkalis [1,2]	6,880±1,305	4,545± 715	10,960± 1,440	7,285± 500	3,130± 255
Alkali-containing high-Btu gas [2]	7,480± 390	7,650± 1,200	11,170± 5,640	7,280± 1,170	[3]2,720
Soaked in alkali solution and dried:					
Fired in air	9,030	3,060	2,940	1,600	1,740
Exposed to alkali-containing high-Btu gas	8,020	3,170	3,830	2,100	1,700
	AA-22	BRIKRAM 90R	ARCO 90	HW-23-75	KX-99
High-Btu gas, no alkalis [1,2]	5,045± 320	12,685± 2,095	20,410± 1,905	11,430± 780	13,880± 1,895
Alkali-containing high-Btu gas [2]	[3]3,610	11,510± 4,300	21,750± 6,370	10,100± 1,530	[3]13,170
Soaked in alkali solution and dried:					
Fired in air	7,100	14,300	26,650	9,430	13,930
Exposed to alkali-containing high-Btu gas	2,090	23,070	24,740	12,040	10,630

[1]Data from table 15, 250 h.

[2]95-pct confidence intervals shown.

[3]Absense of ± indicates that too few measurements were made to adequately establish confidence intervals.

AA-22, LITECAST 75-28, and KX-99, too few test specimens were used to allow a meaningful statistical comparison to be made. When cold crushing strength data in lines 3 and 4 of table 23 are examined, a similar conclusion can be drawn; the presence of alkali vapor did not appear to be harmful.

After a second exposure (250 h), made to produce specimens for hot MOR evaluation, visual inspection of 1- by 1- by 7-in refractory samples failed to reveal any changes in the test specimens. The refractories did show a significant increase in alkali content due to soaking, as is evident from the partial chemical analyses of some of these specimens presented in table 24. Hot MOR values at 980° C for these specimens are listed in table 25. The data indicate that hot strengths of the alkali-impregnated high-alumina castable, the 45-pct-Al_2O_3 brick, and the phosphate-bonded 90-pct-Al_2O_3

ramming mix specimens follow the same trend as cold compressive strengths of identical, but alkali-free, specimens after exposure to the high-Btu gas atmosphere. That is, the alkali-impregnated high-alumina concrete registered a strength loss when compared to identical air-fired specimens, whereas the brick remained unchanged and the ramming mix registered a gain. The alkali-impregnated intermediate-alumina castables did not show significant changes in hot strength following exposure. This last finding contrasts with results from earlier exposure tests (figs. 15-16) of alkali-free specimens. These refractories showed significant increases in cold-crushing strength after exposure to high-Btu gas. These hot MOR results indicate that the presence of alkalis in high-Btu coal gasifier atmospheres may reduce the hot strength of intermediate-alumina refractory concretes in longer term exposures.

TABLE 24. – Potassium and sodium contents of alkali-impregnated refractories exposed to high-Btu gas 2 at 980° C and 1,000 psig for 250 h, weight percent

Treatment	CASTOLAST G		LOABRADE		H.S. BRIKCAST B.F.	
	K_2O	Na_2O	K_2O	Na_2O	K_2O	Na_2O
Prefired in air 980° C for 24 h..	0.01	0.18	0.54	0.28	0.12	0.06
Soaked in 50-wt-pct solution of KOH–NaOH:						
Exposed to high-Btu gas........	2.10	1.40	5	2	ND	ND
Fired in air....................	2.40	1.30	3.9	1.8	ND	ND
Soaked in 25-wt-pct solution of KOH–NaOH:						
Exposed to high-Btu gas........	.84	.71	2.9	1.2	ND	ND
Fired in air	1.10	.78	2.7	1.4	ND	ND
	LITECAST		BRIKRAM 90R		KX-99	
	K_2O	Na_2O	K_2O	Na_2O	K_2O	Na_2O
Prefired in air 980° C for 24 h..	ND	ND	0.02	0.15	ND	ND
Soaked in 50-wt-pct solution of KOH–NaOH:						
Exposed to high-Btu gas........	6	2.6	1.9	.93	2.1	0.62
Fired in air....................	5.7	2.7	2.2	1.1	2.1	.65
Soaked in 25-wt-pct solution of KOH–NaOH:						
Exposed to high-Btu gas........	3.5	1.4	1.5	.72	1.6	.39
Fired in air	3	1.2	1.4	.8	1.3	.29

ND Not determined.

TABLE 25. - Hot MOR at 980° C of alkali-impregnated refractories
exposed to high-Btu gas 2 at 980° C and 1,000 psig for 250 h,
pounds per square inch

Treatment	CASTOLAST	GLOABRADE	H.S. BRIKCAST B.F.
Soaked in 50-wt-pct solution of KOH-NaOH:			
Exposed to high-Btu gas...................	940	500	650
Fired in air[1]............................	2,180	620	630
Soaked in 25-wt-pct solution of KOH-NaOH:			
Exposed to high-Btu gas...................	1,450	720	730
Fired in air.............................	1,680	460	410
Not exposed to alkali:			
Exposed to high-Btu gas...................	ND	730	2,280
Fired in air.............................	ND	680	980
	LITECAST 75-28	BRIKRAM 90R	KX-99
Soaked in 50-wt-pct solution of KOH-NaOH:			
Exposed to high-Btu gas...................	500	1,370	2,880
Fired in air[1]............................	510	1,150	3,330
Soaked in 25-wt-pct solution of KOH-NaOH:			
Exposed to high-Btu gas...................	630	2,780	3,040
Fired in air.............................	820	1,420	2,690
Not exposed to alkali:			
Exposed to high-Btu gas...................	ND	ND	ND
Fired in air.............................	ND	ND	ND

ND Not determined.   [1]Fired in air at 980° C for 250 h.

High-Btu Gas Environment Containing Sodium

To study the effect of the alkali-containing high-Btu gas 2 environment in the GFETC slagging gasifier, a preliminary 50-h exposure at 1,000° C and 360 psig was conducted. Samples of a rebonded fused-grain mullite and a 45-pct-Al_2O_3 brick were either soaked in an NaOH solution or had NaOH crystals or char obtained from the GFETC gasifier packed into holes drilled in the samples. Following this exposure, the mullite refractory containing the NaOH crystals packed into holes showed obvious volume expansion and cracking. XRD analysis revealed that carnegieite and beta-alumina had formed in areas of the mullite refractory that were in contact with the NaOH. (Refractory failure analysis at GFETC determined that the volume expansion associated with the formation of carnegieite and beta-alumina in the fused-grain mullite refractory in the GFETC gasifier was the cause of the refractory failure.) Based on these findings, this mode of exposure was selected for longer term

tests, and the 100-h exposure of the refractories listed in table 26 was conducted. When the test was interrupted for specimen inspection after 50-h exposure time, four magnesia-containing refractories, GUNTAPITE 382, F-264, MAGNEL, and X-13233, were severely damaged and were removed from further testing (figs. 22-23). The fused-grain mullite refractory and the 45-pct-Al_2O_3 fireclay castable were beginning to crack but were exposed for an additional 50 h. Holes in the other specimens were refilled with NaOH, and the exposure test was continued for an additional 50 h.

Postexposure inspection of the remaining refractories revealed that, with the exception of the fused-cast chrome-spinel and the 45-pct-Al_2O_3 brick, all the specimens suffered volume expansion, cracking, or spalling. XRD analyses showed the presence of carnegieite, beta-alumina, gibbsite, or a combination of these minerals in the 60- to 90-pct-Al_2O_3 refractories. The 45- to 50-pct-Al_2O_3 refractories contained trace amounts of carnegieite.

TABLE 26. - Refractories exposed to sodium-containing
high-Btu gas 2 at 1,000° C and 360 psig for 100 h

Trade name	Classification
LABORATORY MIX.............	CA-bonded 90-pct-Al_2O_3 dense castable.
Do.....................	CA-bonded 50-pct-Al_2O_3 dense castable.
KAOCRETE D................	CA-bonded 45-pct-Al_2O_3 dense castable.
HW-23-75..................	Phosphate bonded 60-pct-Al_2O_3 ramming mix.
VALLE 623.................	Phosphate-bonded 80-pct-Al_2O_3 zircon ramming mix.
GUNTAPITE 382.............	Chromate-bonded 90-pct-MgO ramming mix.
F-264.....................	Do.
SR-99.....................	99-pct-Al_2O_3 brick.
RUBY......................	90-pct-Al_2O_3 chrome brick.
CORAL BP..................	80-pct-Al_2O_3 phosphate-bonded, refined brick.
MULFRAX W.................	80-pct-Al_2O_3, rebonded-fused grain mullite brick.
X 13233..................	Mag-Al_2O_3 spinel brick (experimental mix).
MONOFRAX K-3.............	60-pct-Al_2O_3 chrome brick.
UNICHROME................	50-pct-Al_2O_3 Zr-Cr brick.
BISON....................	50-pct-Al_2O_3 brick.
HW 1-77..................	Do.
KX-99...................	45-pct-Al_2O_3 brick.
VARNON BF...............	Do.
MAGNEL..................	90-pct-MgO spinel-bonded brick.
MONOFRAX E..............	Chrome-mag spinel fused-cast brick.

High-Btu Gas Environment Containing Potassium

In the initial 100-h exposure test of refractory specimens to the catalytic coal gasification (CCG) atmosphere (high-Btu gas 4, table 5) at 720° C and 500 psig, potassium was introduced into the system by pumping in an aqueous KOH solution or by placing platinum crucibles containing KOH or KOH-impregnated coal in the sample container. Holes were drilled into some specimens and then filled with KOH-impregnated coal. Introduction of KOH solution directly into the heated chamber resulted in pressure control problems owing to rapid vaporization of the water and resultant sudden pressure increases. The KOH solution feedline (316 stainless steel) running between the outer pressure vessel shell and the base of the heated specimen chamber failed on an average of every 25 to 30 h, causing frequent shutdowns of the system for repairs.

Refractory samples immersed in the crucibles containing KOH were severely attacked, as shown in figure 24. KOH-impregnated refractory specimens with coal-filled holes showed little attack, and refractories exposed only to vapor showed no obvious degradation.

Based on XRD analysis of the material remaining in the platinum crucible after exposure, it appeared that reactions between the KOH and H_2S and CO_2 present in CCG environments occurred rapidly and that the equilibrium partial pressure of potassium compounds present in the vapor may not be that of KOH, but instead that of the carbonate or sulfide. Personnel at the Exxon CCG test facility have also identified carbonates and sulfides in the char produced in the gasification process.

After part of the 310 stainless steel feedline to the test chamber was replced with a heavy-wall pipe, 1- by 1- by 7-in specimens of the four castables listed in table 27 were exposed for 250 h to determine the effect of a potassium-containing CCG environment on the high-temperature properties of these refractories. KOH
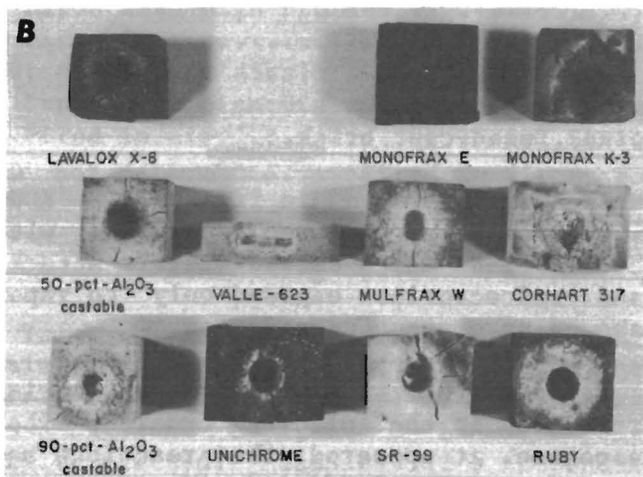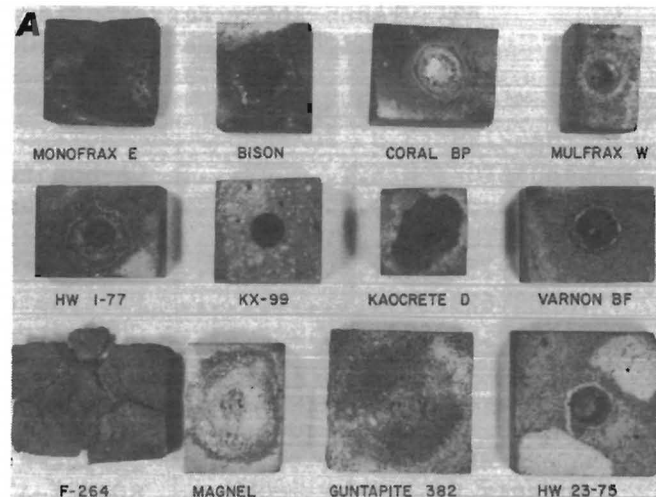
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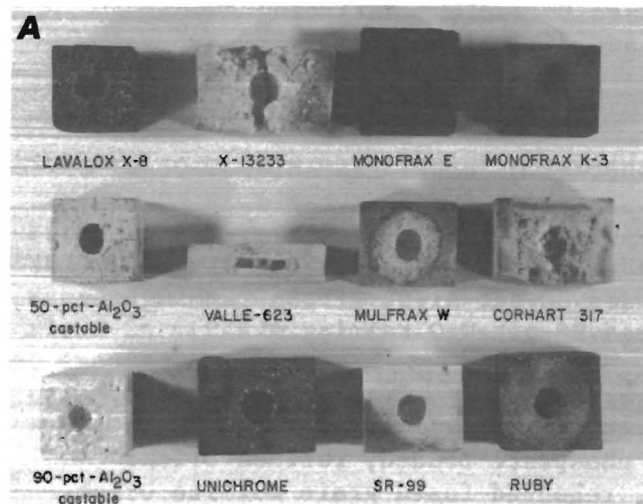
FIGURE 22. - Refractories exposed for (A) 50 h and (B) 100 h to high-Btu gas 2 environment containing sodium at 1,000° C and 360 psig. Holes were refilled with NaOH after first 50 h of exposure.

FIGURE 23. - Additional refractories exposed for (A) 50 h and (B) 100 h (*150 h for KX-99) high-Btu gas 2 environment containing sodium at 1,000° C and 360 psig. Holes were refilled with NaOH after first 50 h of exposure.

solution pumped into the test chamber was used as a source of potassium. Upon examining the specimen container following the test, cracking of the 316 stainless steel feedline was again found, as well as plugging of this line at the point at which it entered the specimen container. The temperature at this point was estimated to be 600° C.

Hot MOR (720° C) strengths of the refractory specimens from this exposure were compared (table 27) to those of

identical specimens air-fired for 250 h at 720° C. A comparison of the MOR values indicated that the 95-pct-Al_2O_3 castable was significantly weaker following exposure to the alkali-containing gas mixture than after firing in air at the same temperature and for the same length of time. Hot strengths of the 55-pct-Al_2O_3 castable after alkali exposure were about the same as those of the air-fired specimens. Both the 45- and the 50-pct-Al_2O_3 concretes made with intermediate-purity CA cement had significantly higher

TABLE 27. - Results of exposing refractories to potassium-containing high-Btu gas 4 at 720° C and 500 psig for 250 h

| Trade name | Classification | Hot MOR, psi[1] | |
		Air fired[2]	High-Btu gas 4 plus CCG char
CASTOLAST G........	CA-bonded 95-pct-Al_2O_3 dense castable.	1,248± 83 ↔	974± 55
LOABRADE..........	CA-bonded 55-pct-Al_2O_3 dense castable.	523±182	890±782
H.S. BRIKCAST B.F..	CA-bonded 50-pct-Al_2O_3 dense castable.	876± 69 ↔	1,146±151
KAOCRETE D........	CA-bonded 45-pct-Al_2O_3 dense castable.	830±125 ↔	1,280±243

[1]95-pct confidence intervals shown. Significant difference at 99-pct confidence level is indicated by "↔".
[2]Fired in air at 720° C for 250 h.

hot strength after exposure to the CCG environment than the air-fired specimens. However, hot MOR (at 720° C) of the 50-pct-Al_2O_3 castable was increased by about

FIGURE 24. - Metal and refractory specimens following exposure to potassium containing high-Btu gas 4 (platinum crucible with KOH) at 720° C and 500 psig.

250 pct following exposure to alkali-free high-Btu gasifier environments (980° C, 1,000 psig, figure 15), but a strength increase of only about 150 pct was noted after exposure to the CCG environment. Chemical analyses of the refractories following the exposures showed a large gain in K_2O content compared to that of the air-fired sample.

Chemical analysis of the steam condensate collected during these exposures showed that K_2O concentration in the steam condensate dropped from about 100 ppm for the initial 8 h of the tests to about 15 ppm after 30 h and to 2 ppm after 80 h, remaining at this level throughout the remainder of the exposure.

A 2,000-h exposure was then conducted at 720° C and 500 psig to provide data on refractory cold compressive strengths after an extended period in the CCG environment. High-Btu gas 4 and alkali vapor in equilibrium with char obtained from Exxon's pilot plant constituted the gaseous environment. The compressive strength data in table 28 indicate that the intermediate-alumina concrete became significantly stronger after exposure to the CCG environment, whereas the strength of high-alumina concrete was lower after exposure. Compressive strengths of the other refractories remained unaffected by the exposure conditions. Similar trends were observed for
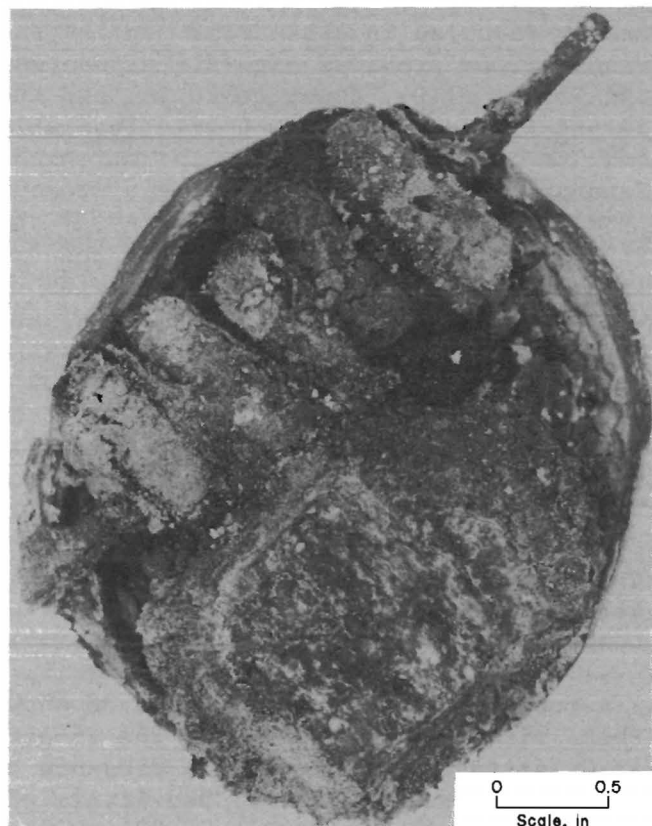
TABLE 28. – Results of exposing refractories to potassium-containing high-Btu gas 4 at 720° C and 500 psig for 2,000 h

Trade name	Classification	Cold crushing strength, psi[1]	
		Air fired[2]	High-Btu gas 4 plus CCG char
CASTOLAST G........	CA-bonded 95-pct-Al_2O_3 dense castable.	9,110 ←→	4,375±1,083
H.S. BRIKCAST B.F..	CA-bonded 50-pct-Al_2O_3 dense castable.	4,275 ←→	10,355±2,995
H.S. BRIKCAST B.F. plus SS FIBERS.	...do................	4,095 ←→	12,025±3,189
BRIKRAM 90R........	Phosphate-bonded 90-pct-Al_2O_3 ramming mix.	11,585	9,600±1,229
KX-99.............	45-pct-Al_2O_3 brick....	9,500	7,515±1,634

[1]Fired in air at 720° C for 2,000 h. Significant difference at 99-pct confidence level is indicated by "←→".
[2]95-pct confidence intervals shown.

the abrasion resistance of the exposed refractories. Chemical analyses of the samples exposed for 2,000 h to CCG vapor indicated that the K_2O content of the castable refractories increased from pre-exposure levels of 0.1 to 0.2 pct to 0.4 to 0.8 pct.

The refractory specimens submerged in CCG char showed signs of degradation at the end of the 2,000-h exposure. These refractories were sectioned, and SEM elemental analyses indicated that potassium had migrated throughout the specimens. There were insufficient samples for strength testing, but the refractories could be broken by hand. No volume expansion was observed.

Exposure to Low-Btu Gas

Two exposures to low-Btu gas were made at 980° C and 400 psig. In the first, several refractories cast from as-received dry mixes were exposed for 250 h. In the second, a few selected refractories cast from commercially available dry mixes, to which small quantities of metal fiber reinforcement had been added, were exposed for 500 h. When the specimens were removed from the sample container at the conclusion of the 250-h low-Btu gas exposure, no visible changes were

noted. As shown in table 29, no significant strength losses were measured. The 45- and 50-pct-Al_2O_3 CA-bonded castables nearly doubled in strength. Unlike the results from previous high-Btu exposures, the 95-pct-Al_2O_3 dense castable and the 90-pct-Al_2O_3 phosphate-bonded castable had no significant loss in strength. Exposure to the low-Btu environment produced no visible changes in any of the SiC brick specimens. Analysis of the exiting gas indicated that the amount of CO was increased at the expense of CH_4 and CO_2, while H_2 was produced by passage through the sample container.

Table 30 gives refractory and metal fiber data and summarizes the effects of the 500-h low-Btu gas exposure on the compressive strength of the metal-fiber-reinforced specimens compared to identical specimens fired in air at the same temperature for the same length of time.

A comparison of tables 29 and 30 shows that with the exception of the 95-pct-Al_2O_3 castable specimens, the presence of metal fiber reinforcement had little effect on the relationship between air-fired and low-Btu-gas-exposed refractory. Significant strength gains occurred in all refractory fiber compositions of the intermediate-alumina dense castables, as

TABLE 29. – Results of exposing refractories to low-Btu gas at 980° C and 400 psig for 250 h

Trade name	Classification	Compressive strength, psi[1]	
		Air fired[2]	Low-Btu gas
CASTOLAST G...	CA-bonded 95-pct-Al_2O_3 dense castable.	9,810± 1,590	9,660± 550
LOABRADE......	CA-bonded 55-pct-Al_2O_3 dense castable.	1,920± 280	2,495± 220
H.S. BRIKCAST B.F.	CA-bonded 50-pct-Al_2O_3 dense castable.	3,090± 270 ↔	7,025± 700
KAOCRETE D....	CA-bonded 45-pct-Al_2O_3 dense castable.	2,285± 295 ↔	6,945±2,425
LITECAST 75-28	CA-bonded 50-pct-Al_2O_3 insulating castable.	1,280± 125 ↔	2,490± 790
CA-25.........	78-pct-Al_2O_3 CA cement................	10,355 810	9,185 1,300
AA-22.........	Phosphate-bonded 90-pct-Al_2O_3 dense castable.	8,105± 630	6,550±1,750
BRIKRAM 90R...	Phosphate-bonded 90-pct-Al_2O_3 ramming mix.	19,145± 1,980	15,615±5,305
HW 23-75......	Phosphate-bonded 60-pct-Al_2O_3 ramming mix.	13,150± 3,035	11,150± 740
ARCO 90.......	90-pct-Al_2O_3 brick....................	18,110±12,340	25,100±8,470
KX-99.........	45-pct-Al_2O_3 brick....................	12,715± 4,810	11,110±1,280
REFRAX 20.....	Silicon-carbide brick.................	ND	ND

ND Not determined.

[1]95-pct confidence intervals shown. Significant difference at 99-pct confidence level is indicated by "↔".

[2]Fired in air at 980° C for 250 h.

TABLE 30. – Results of exposing CA-bonded Al_2O_3 castables containing stainless steel fibers to low-Btu gas at 980° C and 400 psig for 500 h

Refractory	Fiber added, wt pct	Compressive strength, psi[1]	
		Air fired[2]	Low-Btu gas
CASTOLAST G:			
Plus 446 SS fiber......................	2	7,150 ↔	6,020
Plus coated 446 SS fiber.................	2	6,650	5,920
Plus 430 SS fiber......................	2	6,320	5,400
Plus 310 SS fiber......................	2	6,280	5,610
H.S. BRIKCAST B.F.:			
Plus 446 SS fiber......................	4	4,100 ↔	8,560
Plus coated 446 SS fiber.................	4	3,890 ↔	10,580
Plus 430 SS fiber......................	4	3,570 ↔	10,410
Plus 310 SS fiber......................	4	3,370 ↔	9,750
Plus 304 SS fiber......................	4	3,720 ↔	9,960
Plus 430 SS high temperature fiber......	4	3,930 ↔	10,220
KAOCRETE D:			
Plus 446 SS fiber......................	4	5,300 ↔	11,410
Plus coated 446 SS fiber.................	4	4,260 ↔	14,120
Plus 430 SS fiber......................	4	4,130 ↔	12,790
Plus 310 SS fiber......................	4	4,190 ↔	12,530
Plus 304 SS fiber......................	4	4,200 ↔	10,100
Plus 430 SS high temperature fiber......	4	4,570 ↔	12,620
LITECAST 75-28:			
Plus 446 SS fiber......................	4	1,530 ↔	2,840
Plus 304 SS fiber......................	4	1,300 ↔	2,290

[1]Significant difference at 99-pct confidence level is indicated by "↔".

[2]Fired in air at 980° C for 500 h.

well as the intermediate-alumina lightweight insulating castable.

In general, additions of up to 4 wt pct of stainless steel fibers to refractory concretes had no deleterious effect on the cold-crushing strength following exposure to low-Btu gas, even though it contained H_2S. However, in contrast with earlier results in high-Btu environments, there was evidence of metal fiber embrittlement and degradation following the exposure. Metallographic examination of the metal fibers removed from the 45-pct-Al_2O_3 dense castable samples after exposure indicated that the coated 446 fibers showed the least surface corrosion. The remaining fibers were corroded about equally, with 304 fiber showing the most corrosion. Surface microstructures of the different stainless steel fibers following the low-Btu gas exposure are shown in figure 25.
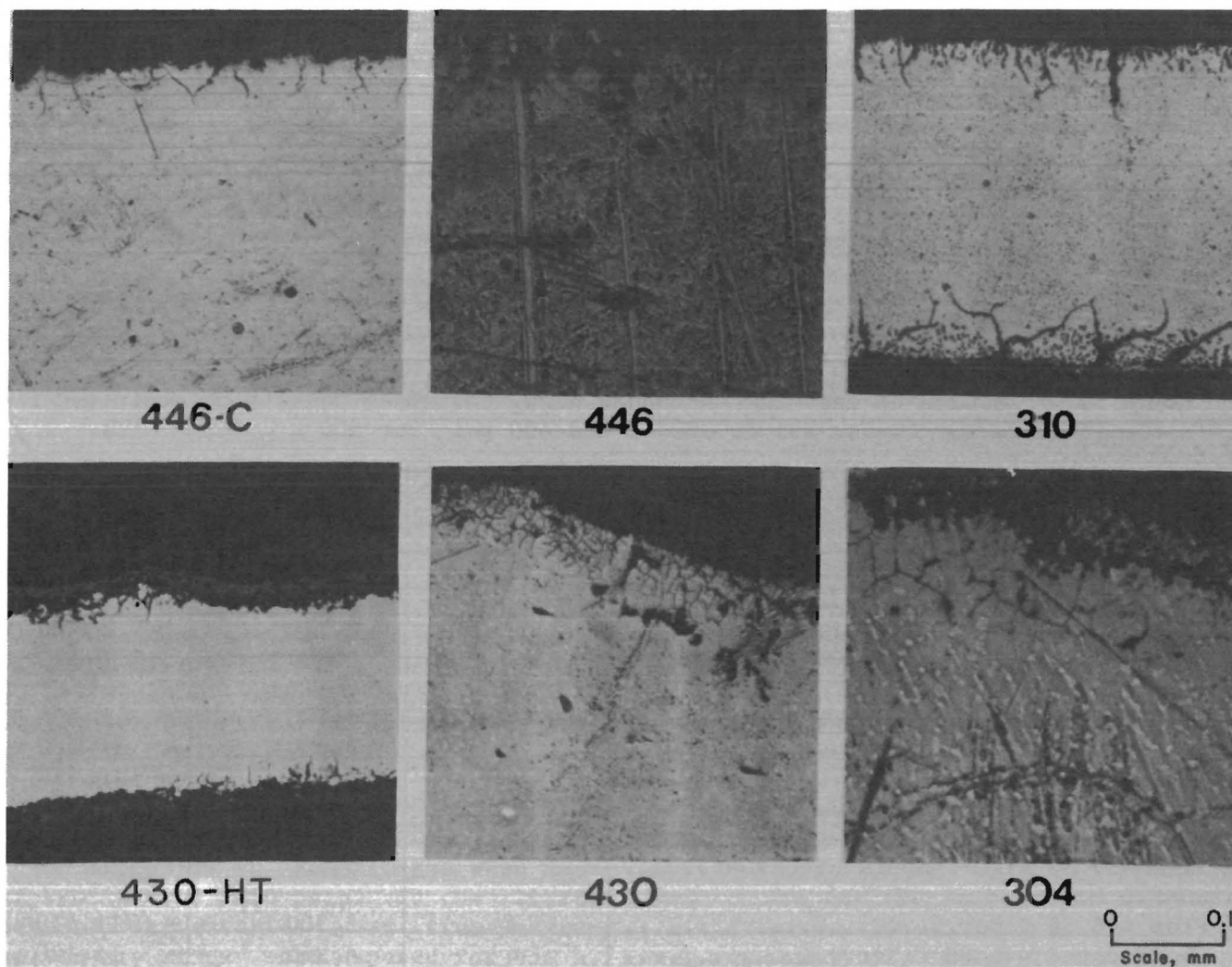

FIGURE 25. - Surface microstructures showing corrosion of different stainless steel reinforcement fibers in 45-pct-Al_2O_3 dense castable following 500-h exposure to low-Btu gas at 980° C and 400 psig.

CONCLUSIONS

Based on the results obtained in this study, the best commercially available monolithic refractories for the hot-face lining of a nonslagging high-Btu gasifier appear to be intermediate-alumina castables made from calcined fireclay aggregate and intermediate-purity CA cement. The best brick appear to be those of intermediate alumina content (45 to 60 pct). Phosphate-bonded alumina-chrome could be used as patching material. The extra cost of using refractory materials of the highest possible alumina content does not appear to be justified. Other conclusions are:

1. At the temperature encountered at the lining hot face, steam and hydrogen are the most reactive components of the high-pressure, high-Btu coal gasifier atmosphere.

2. The magnitude of the strength changes (decrease or increase) after exposure to steam-containing coal gasifier environments increases with increasing partial pressure of steam and increasing gas temperature.

3. The presence of CO in high-Btu gas does not have an adverse effect on strength in any of the refractories evaluated, probably owing to the presence of hydrogen sulfide.

4. High-alumina refractory concretes made from tabular alumina aggregates and high-purity CA cements lose strength when exposed to typical high-pressure, dry-ash coal gasifier atmospheres at temperatures as low as 760° C. These strength losses are associated with marked increases in alumina grain size but little change in mineralogy. Refractory concretes made from intermediate-purity alumina aggregate and high-purity CA cement have somewhat higher strengths after exposure to high-pressure atmospheres containing steam. Intermediate-alumina refractory concrete, consisting of intermediate-purity alumina aggregate bonded with an intermediate-purity CA cement, shows large gains in strength following exposure to high-pressure steam-containing atmospheres. These strength gains are associated with the development of a structure of interlocking mullite grains.

5. Silica loss, caused by vapor-phase transport, from silica-containing refractories is probably not important in high-pressure, high-Btu coal gasifier atmospheres at temperatures below 1,000° C.

6. The presence of alkali vapor in the simulated coal gasifier atmospheres did not cause a reduction in the hot MOR of intermediate-alumina refractory concretes exposed for up to 1,000 h, but the strength gains normally shown by the intermediate-alumina castables following exposure to alkali-free high-Btu gasifier environments do not appear to be as large when alkali vapor is present.

7. SiC refractories fail in high-pressure, high-Btu, steam-containing gasifier atmospheres.

8. Metal fiber reinforcement was not responsible for any increase in gas-induced changes in refractory strength. Some corrosion of the metal fibers themselves was apparent following low-Btu exposure.

9. Changes in strength of refractories caused by exposure to hydrogen or steam at temperatures typical of dry ash gasifiers are essentially complete after a few hundred hours of exposure, except in some phosphate-bonded materials or in some refractories when alkalis are present.

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